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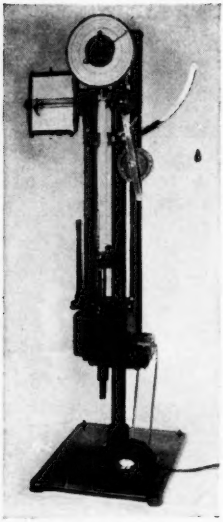

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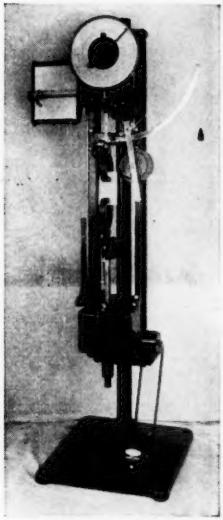

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Relative Affinities of the Anions of Strong Acids for Wool Protein*

By JACINTO STEINHARDT, CHARLES H. FUGITT, and MILTON HARRIS †

A Textile Foundation Publication

Abstract

The fastness of wool dyes to washing varies widely not only among different classes of dyes but even among members of a given class. These variations are manifestations of the differences in affinities of the dyestuffs for the fibers. A possible basis for understanding such differences in affinities was described in two earlier papers in which it was shown that wool immersed in hydrochloric acid solutions combines not only with hydrogen ions but with chloride ions as well. As a consequence of this, it appeared that the affinities for wool of the anions of different acids might vary considerably and that therefore the positions of the titration curves with respect to the pH axis might vary by correspondingly large amounts, according to the acid used. The determination of the titration curve of wool with a gvien acid could then be used to measure the affinity of the anion of the acid for the fiber.

Measurements have therefore been made by Research Associates of the Textile Foundation at the National Bureau of Standards of the combination of wool with nineteen different acids, including, in addition to some of the common mineral acids, several of the simpler aromatic sulfonic, carboxylic, and phenolic acids and a soluble mono-azo acid dye. Wide differences were found between the positions of the resulting nineteen titration curves. A generalized form of the equations previously developed to account for the effect of the concentration of chloride ion on the amounts of hydrochloric acid combined was utilized to calculate the affinity for wool of each of seventeen anions involved. Predictions, based on the equations, as to the effects of variations of anion concentrations and of temperature were tested and confirmed.

* Part of the material in the present paper was presented at the meeting of the American Society of Biological Chemists at New Orleans, Louisiana, in March, 1940.[37]

† Research Associates at the National Bureau of Standards, representing the Textile Foundation.

Measurements of the combination of a number of the same acids with a soluble protein, crystalline egg albumin, were also made. Since qualitatively similar differences in the corresponding titration curves were found with both proteins, it is concluded that the property of combining with anions is not restricted to insoluble proteins, such as wool, but is an inherent property of proteins in general. The affinity of the anions appears to increase with their dimensions, and is higher in aromatic than in aliphatic ions of the same size. These relationships are used as the basis of a consideration of the nature of the forces involved in the binding by proteins of anions, including the anions of acid dyes.

Introduction

IT is well recognized that the fastness of wool dyes to washing, and their related properties of exhausting onto wool or other protein fibers from a dyebath, vary widely not only among different classes of dyes, but also among the members of a given class. These variations are frequently regarded as manifestations of differences in affinity of the various dyestuffs for the fibers. The existence of similar differences in the affinities of ions for proteins in general is suggested by the frequently reported and repeatedly investigated instances of specific differences in the effects of various ions on protein behavior.

A possible basis for understanding such specific effects in terms of the participation of the anions of acids and the cations of bases in the combination of wool protein with acid and base has already been described in two earlier communications.[36, 38] Evidence was presented in support of the view that the combination of wool with hydrochloric acid may be resolved into two partial reactions, one with hydrogen ions and one with chloride ions, and that each reaction is governed by its own equilibrium constant. On the basis of this assumption it proved possible to account for the large effects produced by varying the concentration of potassium chloride on the combination of wool with hydrochloric acid. Among other consequences of this view was a strong possibility that the specific affinities for wool of the anions of different acids might vary considerably, and that therefore the positions of the titration curves of this and other proteins with respect to the pH axis might vary by correspondingly large amounts according to the acid used. The existence of such a variation would constitute critical evidence in support of the hypothesis of anion association, since alternative analyses of the effect of salt, based upon the Donnan membrane-equilibrium equations,[38] offer no obvious basis for the prediction of such an effect.

The present paper describes measurements of the combination of wool with nineteen different acids, ranging in complexity from some of the mineral acids most commonly used in the laboratory through the simpler aromatic, sulfonic, carboxylic, and phenolic acids to a soluble mono-azo acid dye. The acids employed were selected from among those readily available with the purpose in view of obtaining data which could be simply calculated, and interpreted in terms of molecular size, chemical structure, and the effects of specific substituents. For this reason most of the results reported in the present paper deal with acids which are monobasic and virtually totally dissociated in water. A limited number of weak acids which are analogues of some of the strong acids used (e.g., benzoic acid is

analogous with benzenesulfonic acid in the sense used here) have been included for the specific purpose of examining the effects of this analogy. An effort has also been made to include organic acids with all of the more common dissociating groups. Since strong acids containing carboxylic or phenolic radicals as dissociating groups can be obtained only by loading with substituents such as halogens or nitro groups, other related acids have been included in order to make possible an independent appraisal of the effect of various substituent groups, and of more strictly physical factors such as the size and shape of the anion produced.

In order to determine whether differences in affinity between the ions of different acids is restricted to wool, or to the insoluble class of proteins for which the theory of anion-association was specifically proposed,[36] measurements have also been made of the combination of a number of the same acids with a well-characterized *soluble* protein, crystalline egg albumin. Demonstration that the hypothesis of anion association is applicable to both would have an obvious bearing on the interpretation of the titration curves of both classes of proteins and of the wide range of phenomena which depend on the combination of protein with acid or base.

II. Experimental Procedure

Details of the purification of the wool and of the method used in measuring pH values and the amounts of acid combined have already been described.[36, 38]

Additional details which concern the materials used in the present investigation, and modifications of the procedures previously described as well as detailed tables of the experimental data, are given in a more detailed version of this paper published in the Journal of Research of the National Bureau of Standards.

III. Results and Discussion

1. Results Obtained in the Absence of Salts

The results obtained with 16 different strong acids in the absence of salt at 0° C are represented in Fig. 1. In drawing the curves an effort has been made to represent the measurements fairly with smooth curves rather than to preserve the appearance of homogeneity of the data. The resulting tendency of certain neighboring curves to cross or converge is usually within the range of effects which may be ascribed to experimental error.

The most noticeable feature of the data in Fig. 1 is the wide range of positions with respect to the pH coordinates which the titration curves occupy. It is also apparent that except for minor deviations the curves form a coherent family, near neighbors following a fairly parallel course. The change in the slopes of the lower portions of the curves, from the more sharply inflected curve for hydrochloric and ethylsulfuric acids at one end of the pH range to the less sharply inflected curves for picric and flavianic acids at the other end, tends to be gradual and progressive. The appearance of the curves as a group is entirely consistent with the view that they all describe analogous phenomena.

It is a familiar fact that the position on a pH grid of the titration curves of the common weak bases is determined by their own dissociation

constants and not by the dissociation constant or by other chemical properties of the acid employed in the titration. Sets of titration curves obtained with any number of weak or strong acids would be expected to be practically superimposed on one another. Exceptions arise, as in the work of Cannan and Kibrick [7] and of Greenwald [16, 17] with carboxylic acids and phosphates, when the compound formed by the reaction of the base with certain acids is not typically salt-like and does not exist in solution predominantly in the dissociated form. These exceptions find their counterparts, in the case of ampholytes, in the formation of only partially dissociated stoichiometric

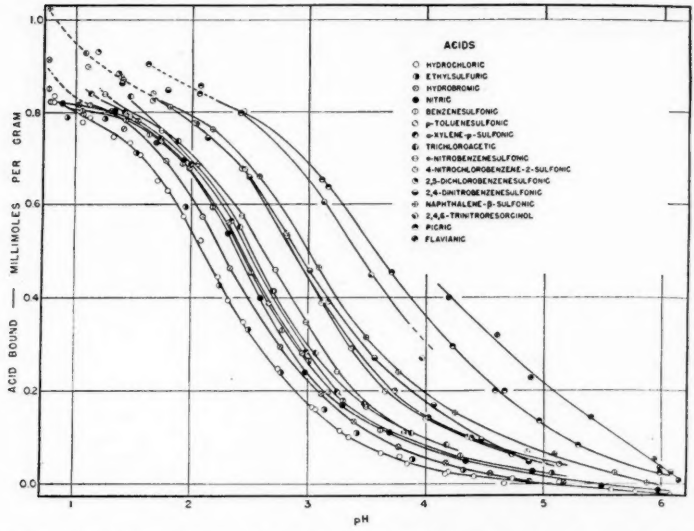

Fig. 1.—The Combination of Wool Protein with Sixteen Different Strong Acids as a Function of pH at 0° C.

The measurements with flavianic acid are represented in milliequivalents instead of millimoles. Points representing the combination of less than 0.14 millimole per g of three acids (*p*-toluenesulfonic, *o*-xylene-*p*-sulfonic, and *o*-nitrobenzenesulfonic) would fall at lower pH values than are required for congruence with the curves for the other acids, and have been omitted to avoid confusing the figure. Data for the two dibasic acids, flavianic and trinitroresorcinol, are only partially represented, as explained elsewhere.

complexes between the anions of the acids and the ampholyte which has combined with hydrogen ions. When these are formed, the positions of the titration curves and to a lesser extent their shapes, will differ according to the extent to which the anion is dissociated.[36]

The wide range of the measurements serves to emphasize the very large differences which may be found when different acids are used. If the position of each curve is characterized by the pH value at which half the maximum amount of acid (about 0.4 millimole per gram) is taken up, there is a difference of almost 2 pH units between the curves shown at the extremes

of the series. Between these extremes the results obtained with the other acids are distributed with a fair degree of uniformity, with no evident tendency to resemble closely the results obtained with hydrochloric acid, the acid which has hitherto been most widely used in measuring the acid-combining properties of proteins.*

Attention must also be directed to another feature of many of the data represented in Fig. 1. This is the combination of amounts of acid in excess of 0.82 millimole per g, the amount reported as the "maximum" obtained with hydrochloric acid. The maximum of 0.82 millimole per g was sometimes exceeded by small amounts when high concentrations of acid (> 0.2 *M*) were used. Measurements of acid combined are susceptible to a relatively large experimental error when such high concentrations of acid are used, because (a) only a small proportion of the acid initially present is combined, (b) some acid hydrolysis of the protein cannot be avoided, and (c) exchanges of water between the partially hydrated fibers and the solutions, difficult to evaluate exactly, have a relatively large influence on the results obtained. For these reasons little weight was placed on these measurements, although they were consistent with the results of similar determinations on bone and hide collagen,[2] and might be explained by the presence in proteins of extremely feeble basic groups, such as the amide groups of glutamine and asparagine, and the large content of peptide nitrogen. Special interest, therefore, attaches to the finding that in every case in which sufficiently high concentrations of other acids are used, a second step in the curve of acid combination apparently begins at pH values more acid than those at which the curve that covers the usually investigated range of combination flattens. Since this fairly well-marked "maximum" of about 0.82 millimole per g has been shown to correspond closely to the primary amino content of the fibers, the additional uptake in more concentrated solutions must be accounted for by the more weakly basic groups or by combination by means of entirely different mechanisms. Such an alternative mechanism is suggested by the titration curve of wool with Orange II at 50°, shown in Fig. 6, in which the excess combination is even larger. The molecules of many dyes are known to be aggregated in aqueous solutions to a greater or lesser extent.[40] Although no evidence suggesting that Orange II is highly aggregated has ever been put forward, the failure of its solutions to obey Beer's law suggests that some degree of aggregation may occur in all but extremely dilute solutions of this dye. Combination of the fiber, at least in part, with aggregated dye anions, might then account for the large amounts taken up, and for the anomalous relation to pH of the amounts combined at high concentrations.

The displacement of the pH range, in which the excess combination with most of the acids is found, removes much of the uncertainty attending the earlier observation of similar excess combination with hydrochloric acid. All three of the possible sources of experimental error mentioned above are reduced or eliminated when the excess combination occurs in the presence of low concentrations of acid. In addition the excess found in concentrated solutions ($1.03 - 0.82 = 0.21$ in the case of napthalene-sulfonic acid) is far outside the limits of experimental error or of the possible range of effects on concentration due to exchange of water between fibers and solution.

* Comparable differences between the titration curves of wool with hydrochloric and with picric acids were found by Elöd.[11]

Although the scatter of the points representing the combination of more than 0.8 millimole per g is considerable, the portions of the curves which represent the second step of acid combination appear to run parallel to one another to about the same extent as do the main curves at higher pH values. The displacements of these parts of the curves thus appear to correspond, qualitatively at least, to the similar displacements of the parts of the curves which represent the combination of the first 0.82 millimole per g. Should further work establish that the concepts applied in this paper to the lower section of the curves may also be employed in the analysis of the excess combination of acid, the possibility is opened of studying in an aqueous environment the combination of these weakly basic groups with acid, and thus determining the number of these groups and the extent of their dissociation.

2. Calculation of the Affinity of Anions for Wool

Any simple analysis of the experimental results in terms of the hypothesis of stoichiometric anion association depends on the assumption that the curve of acid combination is homogeneous, that is, the curve is determined by the combination of hydrogen ions and anions by sets of essentially similar groups in the fiber. If this is not the case, it is meaningless to ascribe shifts in the positions of the titration curves as a whole to variations in a single anion dissociation constant presumed to characterize each protein-anion combination. The assumption is empirically justified when the displacement in the positions of the curves affects all parts of the curves to the same extent. With the minor exceptions noted elsewhere the data in figure 1 appear to justify a treatment based upon such homogeneity.

(a) *Relation of the positions of the titration curves to the anion affinity*

Since it has been assumed that differences in the positions of the curves with respect to the pH axis are determined by differences in K_A', the protein-anion dissociation constant, it is appropriate to attempt to evaluate K_A' for the anions of each of the acids used by means of the position of the corresponding titration curve. The reciprocal of K_A' is referred to hereafter as the anion affinity constant, or simply as the anion affinity.

It has already been shown,[36] that changes in the positions of the titration curves, obtained with a single acid, which are produced by adding different amounts of the anion of the acid in the form of neutral salts can be described by the equation:

$$\text{Fraction of wool combined} \equiv \frac{[WHA + WH^+]}{[WHA] + [WH^+] + [WA^-] + [W^\pm]} = \frac{1}{1 + \frac{K_H'}{a_H}\left(\frac{a_A + K_A'}{a_A + K_A}\right)} \quad (1)$$

in which a_H and a_A represent the activities of the hydrogen-ion and of the anion respectively, the terms containing W represent ionic states of wool, and the constants K_H', K_A', and K_A govern the following hypothetical dis-

sociation equilibria:

$$K_H' \quad WHA \rightleftharpoons WA^- + H^+ \tag{2}$$

$$K_A' \quad WA^- \rightleftharpoons W^{\pm} + A^- \tag{3}$$

$$K_A \quad WHA \rightleftharpoons WH^+ + A^- \tag{4}$$

The constant K_H governing a fourth possible equilibrium:

$$WH^+ \rightleftharpoons W^{\pm} + H^+ \tag{5}$$

does not appear in eq. 1, since it is obvious that the four constants are interrelated by the relation $K_H'K_A' = K_HK_A$.

The assumptions entering into the definition set down in the left hand part of eq. 1 have already been discussed.[30] It has also been shown that each experimental curve is actually somewhat broader (covering a wider range of pH values) than the S-shaped curves described by eq. 1, but that the displacement between curves obtained at different values of a_A are accurately described by the equation.* The difference between the curves is obtained with and without a constant concentration of anions present is also accurately described by converting eq. 1 into the equivalent form, valid when salt is absent:

$$\text{Fraction combined} = \frac{[WHA] + [WH^+]}{[WHA] + [WH^+] + [WA^-] + [W^{\pm}]} = \frac{1}{1 + \frac{K_H'}{a_H}\left[\frac{a_H + K_A'}{a_H + K_A}\right]} \tag{6}$$

The derivation of equations (1) and (6) made clear that their validity is limited to conditions under which the term $[WH^+]$ is greater than the term $[WA^-]$. These conditions are realized, except when much salt is present, when K_A' is greater than K_H. The latter constant has not been evaluated, but it must be considerably larger than K_H', which has been assigned the value 6.3×10^{-5} at 0° C.[26] Thus eq. 6 cannot be used for anions having affinities which result in a displacement of the titration curve by more than 1 or 2 pH units to the right of the position of the curve obtained with hydrochloric acid.

It is possible to derive an equation, similar to eq. 6, which has the complementary condition for validity, i.e., $[WA^-] > [WH^+]$, or $K_A' < K_H$. This equation, applicable to acids with high affinity for wool, is obtained by equating the fraction combined to

$$\frac{[WHA] + [WA^-]}{[WHA] + [WA^-] + [WH^+] + [W^{\pm}]}$$

instead of to

$$\frac{[WHA] + [WH^+]}{[WHA] + [WH^+] + [WA^-] + [W^{\pm}]}$$

* Reasons have been given for attributing this broadening of the experimental curves to the high degree of polyvalency of the wool protein,[30] which has the effect of introducing an empirical exponent on the hydrogen-ion term in the simple equation.[23] The simplified treatment also necessarily leaves out of account all effects due to the mutual interaction of dissociating groups in the molecule except for the effect implied broadly in the inequalities $K_H' < K_H$ and $K_A < K_A'$.

and leads to the general result: *

$$\text{Fraction combined} = \frac{1}{1 + \frac{K_A}{a_A}\left(\frac{a_H + K_H}{a_H + K_H'}\right)} \tag{7}$$

or, in the absence of salt, to the equivalent form:

$$\text{Fraction combined} = \frac{1}{1 + \frac{K_A}{a_H}\left(\frac{a_H + K_H}{a_H + K_H'}\right)} \tag{8}$$

The dependence of the pH coordinate of the midpoint of each curve on K_A' or K_A, in terms of either eq. 6 or 8, may be described by equating the right hand member of each to 0.5. When this is done with eq. 6 the result is

$$K_A' = \frac{a_H(a_H + K_H)}{K_H'} - a_H = \frac{a_H^2 - a_H K_H'}{K_H'} \cdot \frac{K_H}{K_H - a_H} \tag{6'}$$

With eq. 8 the result is

$$K_A' = \frac{K_H}{K_H'} \cdot a_H \left(\frac{a_H + K_H'}{a_H + K_H}\right) \tag{8'}$$

Eqs. 6′ and 8′ both contain constants which have not previously been evaluated (K_A and K_H) as well as the constant K_H' to which the value 6.3×10^{-5} has previously been assigned.† Because of electrostatic requirements, however, $K_H > K_H'$ and $K_A' > K_A$.[36] The ratios between pairs of dissociation constants which differ mainly because of the electrostatic effect of a single charge (such as the first and second dissociation constants of symmetrical dicarboxylic acids) always lie between 10 and 1000. If this analogy is accepted K_H probably lies between $10^{-3.2}$ and $10^{-1.2}$. Since the factor $\frac{K_H}{K_H - a_H}$ in eq. 6′ must be positive, the curve obtained with acids of lower affinity than hydrochloric acid (not reported in this paper) further restricts K_H to values greater than $10^{-2.1}$. The factor thus approaches unity for values of a_H at the midpoints of practically all the curves represented in Fig. 1. Thus, between limits represented by the midpoint of the hydrochloric acid curve and the midpoints of curves for which the condition of validity for eq. 6′ ($K_A' > K_H$) no longer applies, the equation may be simplified to

$$K_A' \doteq \frac{a_H^2 - K_H' a_H}{K_H'} \tag{6''}$$

The corresponding simplification of eq. 8′, valid when $a_H \ll K_H$ (throughout practically the entire range of pH values in which the mid-

* When salt is present, this equation gives the amount of acid *plus salt* combined since the excess negative charge due to $[WA^-]$ may be neutralized in part by adsorbed cations other than hydrogen ions. The amount of salt combined is large only when anions of high affinity are present, or when high concentrations are used, so that the titration curve falls in a region of high pH values.

† In all the calculations that follow the reasonable assumption is made that K_H' is an intrinsic property of the protein, and is not appreciably affected by the nature of the anion combined.[36] (Footnote 18)

points of the curves occur), is

$$K_A' \cong \frac{a_H^2 + K_H' a_H}{K_H'} \qquad (8'')$$

The calculation of K_A', the reciprocal of the affinity, thus depends in either case on an accurate knowledge of K_H', the intrinsic acidity constant of the carboxyl groups of the fiber. By assigning the previously determined approximate value at 0° C to this constant, the relation of K_A' to the pH of the midpoint has been calculated for this temperature according to both equations. The result of this calculation is plotted logarithmically in Fig. 2, in which the midpoint pH, and therefore the value of the affinity constant,

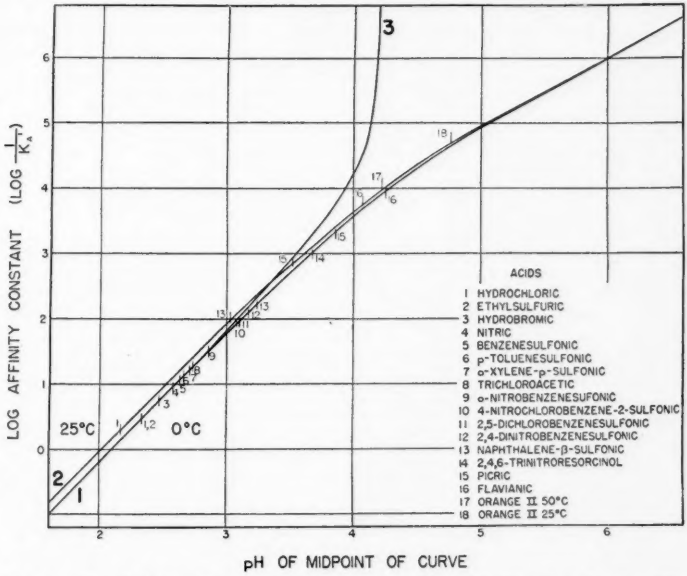

Fig. 2. The Relation Between the Position of the Acid Titration Curve with Respect to pH and the Affinity of the Anion of the Acid for Protein.

Curves 1 and 2 represent eq. 8'' with numerical values of K_H' at 0° C and 25° C respectively inserted. Curve 3 represents eq. 6'' with the numerical value of K_H' at 0° C. Curves 1 and 3 coincide at low pH values.

according to both eq. 6'' and eq. 8'', has been indicated for each of the acids represented in Fig. 1.

It is apparent that in the region of low pH values both equations give practically identical results. The curves approach the same straight line having a slope of 2. In this region the ratio of affinities between two anions is given with a high degree of approximation by the antilogarithm of twice the difference in pH between the midpoints of the titration curves obtained with the acids corresponding to the anions.

At pH values above 3, however, the curves diverge appreciably, and at pH values above 4.2 (pK_H' at 0° C), no physically real values of K_A' are given by eq. 6″. Obviously, however, the conditions under which eq. 6 and 6″ are valid ($K_A' K_H$) are no longer realized when the curves are displaced to such high ranges of pH. Since both equations lead to essentially the same relation between K_A' and midpoint pH in the only range of pH in which eq. 6″ is nearly exact, all calculations of affinity in this paper have been based on eq. 8″, regardless of the range of pH in which the midpoint of a given titration curve may lie.

It should be noticed that as the affinity increases, the difference in the positions of the curves produced by a given increase in affinity becomes larger until ΔpH, which at one extreme is equal to $-\frac{1}{2}\Delta pK_A'$ at the other extreme approaches $-\Delta pK_A'$. As the latter limit is approached closely, the affinity constant becomes independent of the value assigned to K_H' and is equal to the midpoint a_H. It will be shown later that the affinities of commercial acid dyes probably fall in this range; thus, the comparison of their affinities relative to one another may be much simplified.

Included in Fig. 2 is a third curve, also representing eq. 8″, in which the value 9.32×10^{-3} has been used for K_H' instead of the value 6.30×10^{-5}. This curve shows the relation between midpoint pH and log K_A', at a temperature of 25°,[38] and also illustrates the relatively large effect of variations in K_H' on the estimation of K_A' when the latter is large, and the virtual absence of this effect when the latter is small.

By making use of the curve which represents eq. 8″ at 0° C, values of K_A' which correspond to each of the acids represented in Fig. 1 have been determined. These values are given in the fifth column of Table 1. The ion with least affinity, chloride, has a value of K_A', 0.35; picrate, the most tightly bound monovalent ion studied at this temperature, has an affinity almost one thousand times as great as that of chloride, and the divalent flavianate ion has an affinity still higher.* It is apparent from the results summarized in Table 1 that the affinity of the anion tends to rise as the molecular weight increases, but the tendency is not regular and exceptions in the series occur.

Since the experimental curves are broader than those predicted by the much simplified equations, the use of the equations in analyzing the shifts in position of the curves would be rendered more significant, if the progressive change in their slopes could also be shown to be a consequence of the same differences in K_A' which result in their displacements to progressively higher pH values. This demonstration has been made by substituting representative numerical values in eqs. 6 and 8. For the sake of definiteness, the value, 0.01 has been assigned to the ratio $\frac{K_H'}{K_H}$ which has been shown to have a range of reasonable values of 0.01 to 0.001. The result of this calculation with six different values of K_A' is shown in Fig. 3. The calculated curves simulate the curves drawn through the experimental data not only in the relation between the magnitudes of their displacements from one another, but also in the relation of their slopes. Thus, the curves representing low values of K_A' (high affinities) are everywhere less steep than those which correspond to high values of K_A' (low affinities). The progressive change in slope at the midpoints of the experimental curves is in the same

* For comparison, the affinity of the divalent flavianate ion is expressed in the same units as the affinities of the monovalent acids in the table.

TABLE 1.—CALCULATION OF ANION AFFINITY CONSTANTS ($1/K_A'$) AT 0° C

Acid	Molecular weight	pH of midpoint	$-\log K_A'$ from eq. 8''	K_A'	Affinity relative to aff. of chloride ion	pH at which curve crosses HCl 0.1 Molal curve	Affinity relative to aff. of chloride ion (method of crossing point)
Hydrochloric	36.5	2.33	0.45	0.35			
Ethylsulfuric	126.1						
Hydrobromic	80.9	2.47	0.74	0.18	1.9		
Nitric	63.0	2.58	0.96	0.11	3.2	1.71	3.9
Benzenesulfonic	158.2	2.63	1.05	0.089	3.9	1.71	3.9
p-Toluenesulfonic	172.2	2.66	1.10	0.080	4.4	1.73	4.1
o-Xylene-*p*-sulfonic	186.2	2.71	1.21	0.062	5.6	1.83	5.2
Trichloroacetic	163.4	2.73	1.25	0.056	6.2	1.93	6.6
o-Nitrobenzenesulfonic	203.2	2.86	1.50	0.032	11.0	2.05	8.6
4-Nitrochlorobenzene-2-sulfonic	237.6	3.08	1.93	0.0118	29.7	2.68	36.8
2,5-Dichlorobenzenesulfonic	227.1	3.09	1.95	0.0112	31.2	2.68	36.8
2,4-Dinitrobenzenesulfonic	248.2	3.17	2.09	0.0081	43	2.82	51
Naphthalene-β-sulfonic	208.2	3.24	2.23	0.0059	59	3.05	86
2,4,6-Trinitroresorcinol	245.1	3.67	3.02	0.00096	366		
Picric	229.1	3.86	3.34	0.00046	758		
Flavianic	314.2	4.24	†3.94	†0.000115	†3020		

† Calculated, for comparison, as if the anion were monovalent. Since equilibrium was not attained in 23 days, the relative affinity reported is minimal.

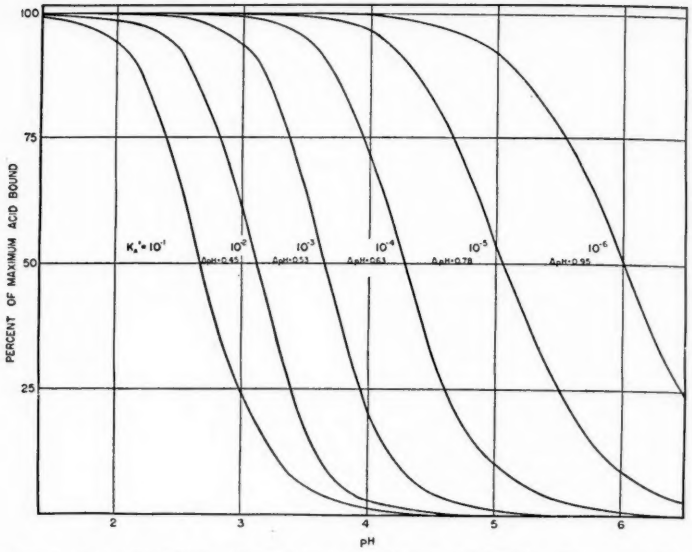

Fig. 3. The Dependence of the Slope of Theoretical Titration Curves on the Protein-anion Dissociation Constant.

The two left-most curves are calculated from eq. 6 and the others from eq. 8. The change from eq. 6 to eq. 8 between $K_A' = .01$ and $K_A' = .001$ has been made in order to preserve consistency with the assumption $\frac{K_H'}{K_H} = .01$.

direction. The qualitative agreement with experiment of these calculations would not be altered by the assignment of other reasonable numerical values to the ratio $\frac{K_H'}{K_H}$.

(b) *Alternative method of calculating relative anion affinities*

In the 6th column of Table 1 is given the ratio of the affinity of the anion of each acid to that of chloride ion. This has been tabulated because the same relative affinity factor may be calculated directly from the experimental results represented in Fig. 1 by combining them with the data for hydrochloric acid at constant chloride concentrations in an earlier paper.[36] The values so obtained thus do not depend on the equations just used.

This alternative method of calculation is made possible by the fact that curves obtained in the presence of constant anion concentrations are less steep than those obtained in the absence of salt and therefore cover a wider range of pH values. Thus, for example, a curve representing results obtained with hydrochloric acid at a constant concentration (0.1 *M*) of chloride ions would intersect all of the curves represented in Fig. 1 with the exception of the curve for flavianic acid. The intersections with the

curves for hydrobromic acid and picric acid would occur so near the extremes of the 0.1 *M* curve that they are not well suited to the present calculation but all of the other intersections may be used. At the point of intersection of the 0.1 *M* hydrochloric acid curve with any curve in Fig. 1 the same amounts of two different acids are bound by the wool at the same pH. The same degree of combination with two different anions is thus brought about by the presence of different amounts of the respective anions by virtue of the difference of affinity for wool characterizing these anions. It follows from the range of ratios of K_H'/K_H which has been adopted elsewhere that the ratio of the activities of the two anions in the two different experiments is inversely proportional to the ratio of the respective anion affinity constants. The anion affinity ratios which are obtained should be the same as those given in column 6 of Table 1.

The activity of potassium chloride at 0.1 *M* at 0° is 0.0768.[18] The assumption has been made that the activity of the anion in each experiment made in the absence of salt is equal to the activity of the hydrogen ion. It is very unlikely that this assumption is true, but the experimental value, pH, is related to the activities of both ions and methods of obtaining individual ion activities are at present unknown. By dividing 0.0768 by the antilogarithm of the negative of the pH, the values given in the last column of Table 1 have been obtained. In view of the fact that the intersecting curves were drawn freehand and that the two kinds of data were obtained with different lots of wool, the agreement of the values in the last column with those in column 6 is satisfactorily close.*

3. Results Obtained in the Presence of Salt

It should be possible to predict the displacements that would be found if the same acids were used in the presence of constant concentrations of their anions, added as neutral salts. By starting with eqs. 1 and 7 instead of eqs. 6 and 8, and making the same simplification which was carried out in arriving at eqs. 6″ and 8″, formulas which give the relation between K_A' and the midpoint pH when the measurements are made in the presence of any constant concentration of anions are obtained:

$$K_A' = a_A \frac{a_H - K_H'}{K_H'} \qquad (1'')$$

$$K_A' = a_A \frac{a_H + K_H'}{K_H'} \qquad (7'')$$

In these equations the quadratic term a_H^2, found in eqs. 6″ and 8″, does not appear. In the range of relatively low affinities, therefore, a given change in K_A' will, in the presence of constant anion concentrations, produce twice the pH change which corresponds to this change in K_A' in the absence of salt. With anions having higher affinities, however, displacements in midpoint pH values obtained in the presence and absence of salt will differ by

* A third method of calculating relative affinities has also been made use of. Mixtures of acids have been equilibrated with wool, and the relative amounts of the two acids combining have been determined. The relative affinities of the two anions calculated from this ratio agree closely with the results of the methods described in this paper. Since the method has thus far been applied to experiments with acids for which no data are given in the present paper, and since work with these acids is still in progress, no examples of these calculations are given here.

less than a factor of 2. These predictions have been tested by making measurements with a number of the acids included in Table 1, in the presence of 0.1 *M* concentrations of their anions, added as the potassium salts. The results of these titrations are represented graphically in Fig. 4. As the figure shows clearly, the differences in the pH values of the midpoints

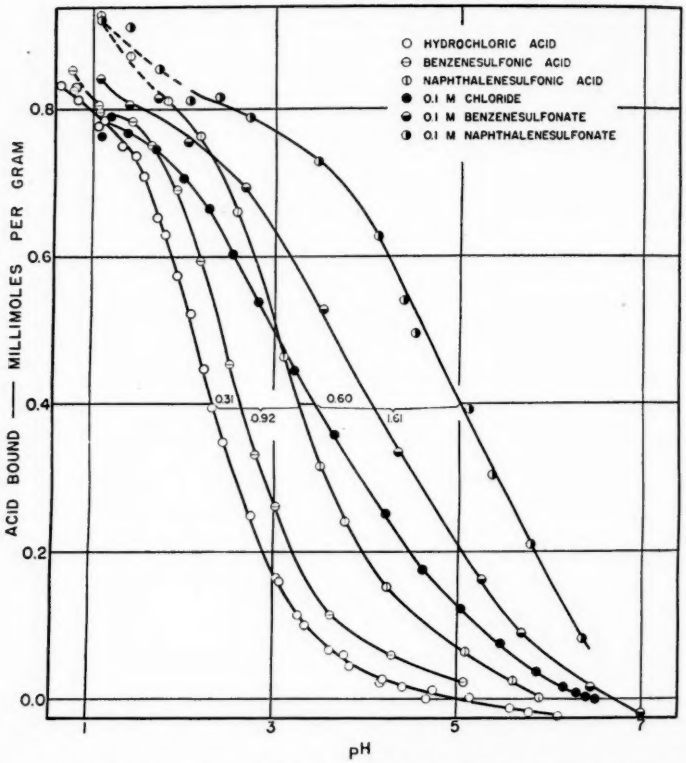

Fig. 4. A Comparison of the Titration Curve of Wool Protein Obtained with Three Different Acids in the Absence of Salt at 0° C, with the Curves Obtained at the Same Temperature in the Presence of a Constant Concentration (0.1 *M*) of the Anions of the Acids.

of the hydrochloric acid and benzenesulfonic acid curves are twice as great for curves obtained in the presence of salt as for those obtained in its absence. The differences between the midpoints of the hydrochloric acid and naphthalenesulfonic acid curves are somewhat less than twice as great in the presence of salt as in its absence. Both differences thus agree with the predictions of the equations.

Similar experiments have also been made at 25° C with Orange II in the presence of a constant concentration of its colored anion, added as the sodium salt. The affinity of this anion is so great, that it combines with the protein in considerable amounts at pH values at which only small amounts of hydrogen ion are normally taken up. The resulting negative charge on the fiber is neutralized, as in all the cases covered by eqs. 7 and 8, by adsorption of positive ions. In the presence of salt, appreciable quantities of sodium ions, as well as hydrogen ions, are bound. Thus, eq. 7 no longer gives the amount of acid taken up alone, but the sum of the amounts of acid and of salt. Since the analysis of these data thus requires the development of a technique for the accurate estimation of this sum, the data obtained with Orange II at a constant concentration of its anion are not included in the present paper. The great steepness of the 0.1 *M* naphthalenesulfonate curve in Fig. 4 is due, in part, to combination with small amounts of salt at high pH values. These should have been added to the amounts of acid combined in order that the resulting curve should be described by eq. 7.

4. Effect of Temperature on Anion Affinity

It has been shown earlier,[38] that a comparison of titration data obtained at two different temperatures permits an estimation of heat changes accompanying the dissociation of the protein-anion complex. Measurements at 25° C have therefore been made with four acids of widely different affinities. The results, represented in Fig. 5, together with the 0° data for three of the acids, also provide a basis of comparison for acids which it is impractical to investigate at 0° C. Results obtained at 25° C with one such acid, Orange II, are also included in the figure. As the figure makes clear, the effect of temperature on the position with respect to pH of the curves obtained with picric acid (0.34 pH unit) is considerably greater than its effect on the curves for naphthalenesulfonic acid (0.21 unit) which in turn show a greater affect than the curves for hydrochloric acid (0.16 unit). No estimate is attempted of the effect of temperature on the position of curves for flavianic acid, since the data obtained at 0° C with this acid probably did not represent final equilibrium.

The curve at 25° C for flavianic acid requires further explanation. When plotted, as in Fig. 5, as *milliequivalents* per gram against pH, the data run nearly parallel to those for picric acid at the same temperature up to values of acid combined of at least 0.65 millimole per g. This furnishes a very strong indication that in this range of pH values the flavianate ions combining with the wool are predominantly doubly ionized, and effectively neutralize two of the positively charged basic groups in the protein. At lower pH values where the data are represented by a broken line, the proportion of the total flavianic acid which is doubly dissociated is so small that a part of the ions which combine with the fiber are monovalent. In the most concentrated solutions combination with the fiber takes place almost entirely with the monovalent ion, so that a plateau at 0.82 *millimole* rather than at 0.82 *milliequivalent* would presumably be found. Since the concentration of flavianic acid is extremely low in the range of pH in which all the ions are predominantly dibasic, it is clear that the affinity of the doubly charged anion is considerably higher than that of the monovalent ion. Trinitroresorcinol also combines with wool as a dibasic acid, when present

in greater dilution. To avoid complicating Fig. 1 only the measurements representing the monobasic function of this acid were included in the figure. Similar effects appear to characterize sulfuric acid.[34]

The affinities at 25° C of the acids represented in Fig. 5, calculated from eq. 8″, are given in the first part of Table 2. The values of K_A' listed

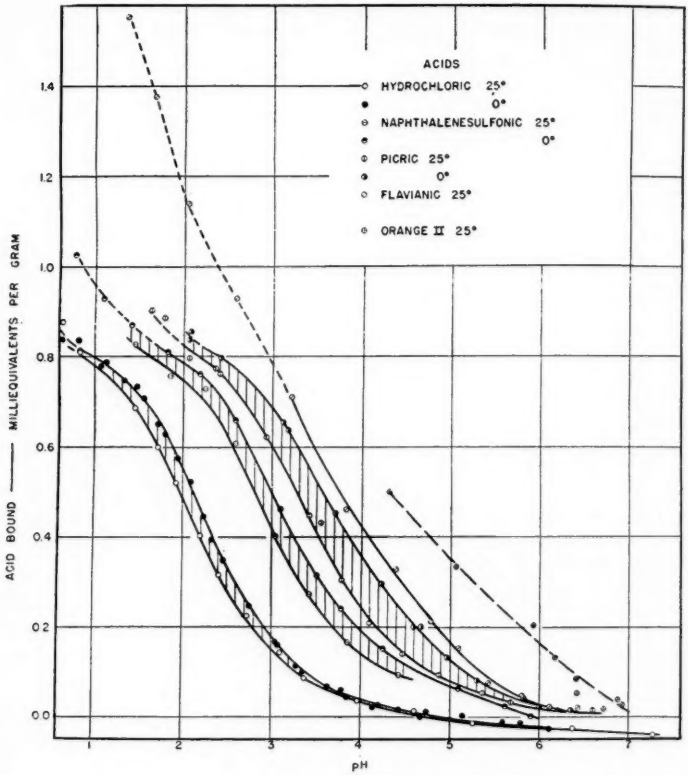

Fig. 5. A Comparison of the Titration Curves of Wool with Various Acids at 0° C and 25° C.

in column 4 were obtained graphically from the curve for 25° in Fig. 2. Thus the effect of temperature on K_H' has been taken into account. Owing to the inclusion of data for Orange II, the differences of affinity comprised in this table cover almost eight times as wide a range as those listed in Table 1.

TABLE 2.—CALCULATION OF ANION AFFINITY CONSTANTS AND HEATS OF DISSOCIATION AT 25° AND 50° C

Acid	pH of midpoint	$-\log K_A'$ from eq. 8''	K_A'	Affinity relative to aff. of chloride	$\left(\frac{K_A'}{K_A'}\right)_0^{25}$	Average heat of dissociation of anion from wool in temperature interval 0–25
		25°				*calories per mole*
Hydrochloric	2.16	0.31	0.49		1.40	2170
Naphthalene-β-sulfonic	3.03	1.97	.0107	46	1.81	3850
Picric	3.52	2.89	.00129	380	2.80	6670
Flavianic	4.07	**3.77	.000170	2880		
*Orange II	4.76	4.68	.000021	23400		
		50°			$\left(\frac{K_A'}{K_A'}\right)_{25}^{50}$	ΔH_{25}^{50}
Hydrochloric	2.21	0.38	0.42		0.85	−1630
*Orange II	4.21	3.97	.000107	3900	†5.09	†12500

* Molecular weight 328.3.

** Expressed for purposes of comparison as if the anion were monovalent.

† The Orange II data at 25° C do not represent equilibrium values. Thus the relative affinity given for this temperature, and the value of ΔH_{25}^{50} are minimal.

The sixth column of the table gives the ratio of the protein-anion dissociation constants at 25° and 0°. From this ratio, and the van't Hoff equation, the average heat of dissociation in this range of temperature has been calculated. The values so obtained are given in the last column. The heats of dissociation rise from some 2000 calories in the case of chloride ion to nearly 7000 calories in the case of picrate. As should be expected more energy is required to dissociate the more tightly bound ions.*

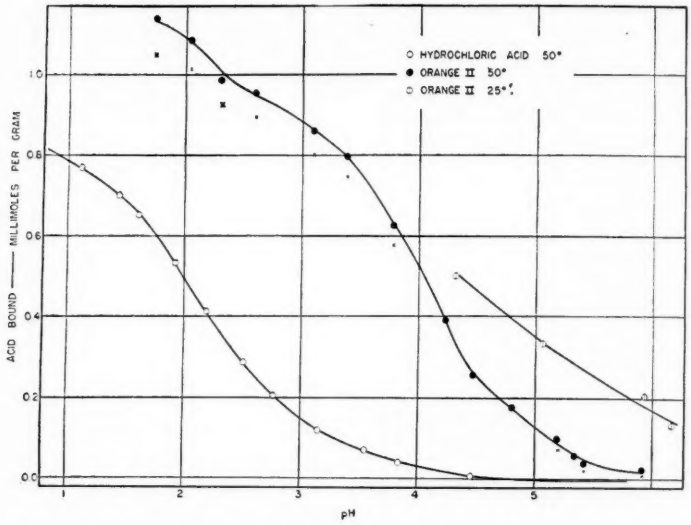

Fig. 6. The Combination of Wool Protein with the Azodye Acid Orange II, and with Hydrochloric Acid as a Function of pH at 50° C.

The significance of the crosses is explained in the text. For comparison, data obtained with Orange II at 25° C are included.

In order to evaluate the effect of temperature on the affinity of Orange II, the amounts of this acid combined by wool were also measured at 50° C, after allowing a period of 5 days for the attainment of equilibrium. The results, together with data for hydrochloric acid at the same temperature are represented graphically in Fig. 6. The maximum amounts combined are in fair agreement with those reported for high concentrations of this dye by Ender and Müller.[12] Included in the figure for the purpose of comparison are the data obtained with Orange II at 25° C. The measurements represented by crosses were obtained at 50° C by determining the increase

* The value of K_H' at 25° was chosen on the basis of the earlier analysis of the effect of temperature on the combination of wool with hydrochloric acid,[38] in which it was assumed that the heat of transfer of the ions from the solution to the fiber could be neglected. The heats of dissociation given in the table may therefore be subject to a small correction. Since this correction would be practically invariant, its application would not affect the relative order of the heats of dissociation, nor the great differences between them.

in dry weight of the fibers as the result of combination with dye. The small discrepancies between the two sets of results (larger the more acid the solution) are accounted for by the fact that small amounts of amide nitrogen are split off, as a result of the prolonged exposure to dye at this temperature, and affect the apparent dye-uptake estimated from the difference in the acid titer of the dye bath brought about by the wool. The amounts of ammonia produced by comparable exposure to the same concentrations of hydrochloric acid are considerably smaller.

A comparison of the titration curve obtained with Orange II at 50° C with the portion of the curve obtained at 25° C strongly suggests that the data for the lower temperature do not represent a final equilibrium state. This was clearly the case when higher concentrations of dye were used at 25° C; combination of dye in 35 days at this temperature in no case exceeded 0.63 millimole, even when solutions more acid than those used at 50° C were employed. The affinity of the dye anion at 25° (listed in the first part of table 2) must therefore be regarded as minimal. Thus, the heat of dissociation of the dye anions is even larger than the value in the table (12,500 calories), and exceeds by a large factor the heats of dissociation of the other ions listed. This large value also suggests an explanation of why the *rates* of dyeing and of stripping are so much affected by temperature. Since the anions are held much more loosely at elevated temperatures (the factor is greater than 5 in the interval 25° C–50° C), they are more readily passed on from one combining group in the fiber to another, toward the innermost parts of the fiber from the peripheral portions which are first dyed, or in the stripping process in the opposite direction.

IV. Combination of Anions with a Dissolved Protein

If it can be shown that stoichiometric combination with anions occurs in the reaction of both soluble and insoluble proteins with acids, there is a wide range of application in which it must be taken into account.* If it occurs only with wool or with the fibrous proteins † the distinction must be regarded as a clue to the nature of the specific structural differences between soluble and insoluble proteins.

To determine whether the marked differences in the titration curves of wool obtained with different acids are also to be found with dissolved proteins, determinations were made of titration curves of the soluble protein, egg albumin, with several of the same acids. The results of these measurements at 22° C are shown in Fig. 7. The position of the broken line at the top of this figure, inserted for reference, shows the maximum acid-binding capacity, indicated by the work of Kekwick and Cannan with hydrochloric acid.[22] The crosses distinguish measurements in which incipient precipitation was indicated by a faint opalescence. In every case measurements with higher concentrations of the acid produced a visible

* Examples are (a) the calculation of Donnan membrane potentials or ion-distribution ratios, in which disagreement with experiment often appears [3, 4] unless combination with ions other than H^+ and OH^- is taken into account; [1] (b) the possibility of forming physiologically significant weakly dissociated protein complexes such as with calcium.[10]

† The amounts of acid or base combined with *silk* at any pH [12] have the same first-order dependence on the concentration of anions and cations, respectively, that characterizes wool.

precipitate, and have been omitted from both the table and the figure, to avoid all possibility that the effects described may have been due, in whole or in part, to the existence of two macroscopic phases.

The differences between the curves shown in Fig. 7 obviously correspond to the differences found with wool. With one exception, the affinities of the anions for egg albumin are in the same order as their affinities for wool. One difference, however, distinguishes the two sets of data. The positions of points along the curves for egg albumin show no tendency to remain

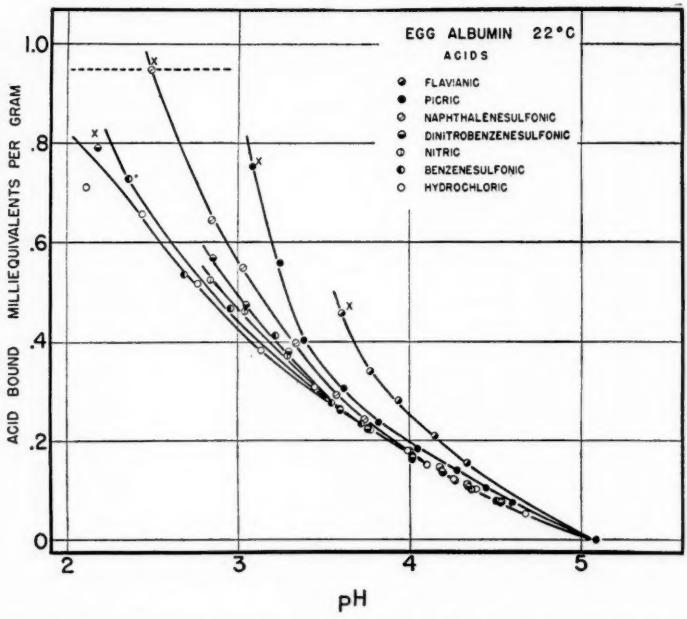

Fig. 7. The Combination of a Dissolved Protein, Egg Albumin, with Various Strong Acids as a function of pH.

The significance of the crosses is explained in the text.

equidistant with respect to the pH axis; neighboring curves converge strongly as decreasing amounts of acid are bound. The convergence may be regarded as a consequence of the excess of carboxyl groups over amino groups in the dissolved protein. Because of this inequality only a part of the carboxyl groups are ionized in the uncombined state, and this part alone is free to accept hydrogen ions from the acids. The complete titration curve of all the carboxyl groups of the protein extends beyond the isoionic point and can only be obtained by titration with base as well as with acid. The part of the carboxyl curve which is obtained by combina-

tion with base in the absence of salt is not governed by the affinity properties of anions, since the cations of bases rather than the anions of acids are present when it is obtained. Thus, unless salt is present, the influence of the anion disappears entirely at the point of zero combination with acid. This circumstance tends to obscure the simplicity of the theoretical relation between the affinity of the anion and the pH coordinates of acid titration curves. This simplicity will manifest itself only when the acid combination curve coincides with the titration curve of the carboxyl groups as a whole, as it does with wool. With salt present a secondary effect of the anion beyond the point of zero combination may be observed, as the data of Briggs [5] obtained on serum albumin with metaphosphate plainly show.

Since the curves in Fig. 7 converge sharply it is difficult to compare the absolute magnitudes of the differences in affinity of the several anions, with the corresponding differences found with wool. Obviously the comparison should be made between solutions which are as far as possible from the isoionic point in order to minimize the effects of the convergence. The data do not extend to very acid solutions, but at the extreme of the range represented the differences in the pH coordinates of the curves approach values only slightly smaller than the differences between curves for the same acids in Fig. 1.*

Since the theory of stoichiometric anion combination was originally formulated to account for the large effects of the presence of salt on the hydrochloric acid combination curves of wool, the application of this theory to the much smaller salt effects described by Cannan for egg albumin [6] seemed at first uncalled for. The experiments just described, however, suggest that the difference between the titration curves of dissolved and undissolved proteins in the absence of salt [36] cannot be due to the failure of anions to combine with the dissolved protein. The contradiction between the results of the two kinds of experiments is only apparent, since the existence of a stoichiometric salt effect is not an inevitable consequence of every situation to which eq. 1 may be applied. Such salt effects are found only when $K_A' \gg a_A \gg K_A$. When K_A' and K_A are both very large, the bracketed term in the denominator of eq. 1 approaches a constant and is nearly independent of a_A. When both constants are very small, the bracketed term approaches unity and is again nearly independent of a_A. In either case (corresponding to extremely low or extremely high affinity of anions for the protein) the availability of hydrogen ions rather than of anions becomes the factor limiting the extent of combination with acid. Thus, as in the case of egg albumin, the titration curve obtained in the absence of salt will not differ greatly from those obtained at constant anion concentrations.

In view of the numerous indications that dissolved proteins do combine with such commonly employed anions as chloride, acetate, and phosphate,

* Results of the kind described for both proteins may furnish a basis for explanations of the many reports of ion specificity in the literature of protein and enzyme chemistry. Attempts have been made to deal with some of these specific properties, such as differences in salting-out effectiveness, by treatment of the electrostatic interaction between ions having different sizes, shapes and electric moments. Many phenomena of specificity remain, however, for which plausible explanations, based on simple electrostatic considerations alone, are not easily obtained. Among these are numerous instances of differences in the electrophoretic mobility of various proteins when different anions or different concentrations of anions are present in buffers,[9, 14, 31, 29] and large-scale differences in the effectiveness of various anions in environments producing protein denaturation.[15, 35]

but not to an extent comparable to their combination with hydrogen ions in acid solutions,[1, 3, 14, 39] the first of the two alternatives (K_A' and K_A large) probably applies in the case of these simpler ions. The difference in the absolute values of these constants characterizing the soluble and insoluble proteins may be related to the structural factors responsible for the differences in their respective states of dispersion.

It should be noted in Fig. 7 that precipitation occurred at concentrations which were in the inverse order of the affinities. Picrate and flavianate are ions having a high precipitating efficiency for proteins, but many others, such as tannate and metaphosphate, are equally well known.[28, 29, 26, 5] It would be of interest to determine to what extent protein precipitation by specific reagents, such as picrate or tannate, and the salting out of proteins with various salts may be regarded as manifestations of the same general protein-anion equilibrium. When the affinity is so great that the presence of only small amounts suffices to cause combination and precipitation the anion or acid is naturally described as a specific protein precipitant. When the affinity is low and large excesses are required, the combination and precipitation may have many of the characteristics associated with salting-out. With extremely low affinities, such as that of chloride, salting out is often not practicable.

V. The Relation of Anion Affinity to Size, Structure and Basicity of Ions

If the phenomena reported in the present paper are to be ascribed to the formation of partially dissociated protein-anion combinations, it is logical to enquire into the nature of the forces which confer so wide a range of affinities for protein to different ions. The existence in certain kinds of solutions of ion combinations which are only partially dissociated is now well established.[7, 24] Such combinations may be formed in two possible ways, involving either directed or undirected valence forces. The first alternative involves the formation of a bond having partially covalent nature, or a hydrogen bond; the second comprises various kinds of polar forces, whether electrostatic (coulombic) in nature or otherwise and includes van der Waals forces. If the first type is involved the principal relation found among the anions should be an inverse one of affinity to the intrinsic strength of the acid.* The relations found in cases to which the second alternative applies would be expected to be more complex.

Since most of the acids included in the present research are of approximately equal strengths in water, but differ widely in affinity, the first alternative seems to have little in its favor. Nevertheless, a *part* of the total binding energy between anion and protein might still be due to the formation of a directed bond, especially since the intrinsic strengths of the various acids, as distinguished from their apparent strengths in water, are not all equal.

In an effort to appraise more closely the influence of the basicity of the anion on the affinity, comparisons (Fig. 8) have been made of the results obtained with pairs of closely similar acids, such as benzenesulfonic

* Here the possibility of the formation of a bond between the protein and the charged group of the anion (when the anion is polyatomic) is alone under consideration.

and benzoic acids, which differ widely in strength. The data shown are limited to ranges of pH in which the concentration of the undissociated form of the weak acid does not exceed 0.1 *M*, in order to avoid effects, due to the presence of larger amounts, which have been described elsewhere.[27] There is very little difference between the amounts of strong and of weak acid combined at a given pH in the case of the benzenesulfonic-benzoic acid comparison. On the other hand, the anion of dinitrophenol appears to have a definitely higher affinity for wool than the anion of its totally dis-

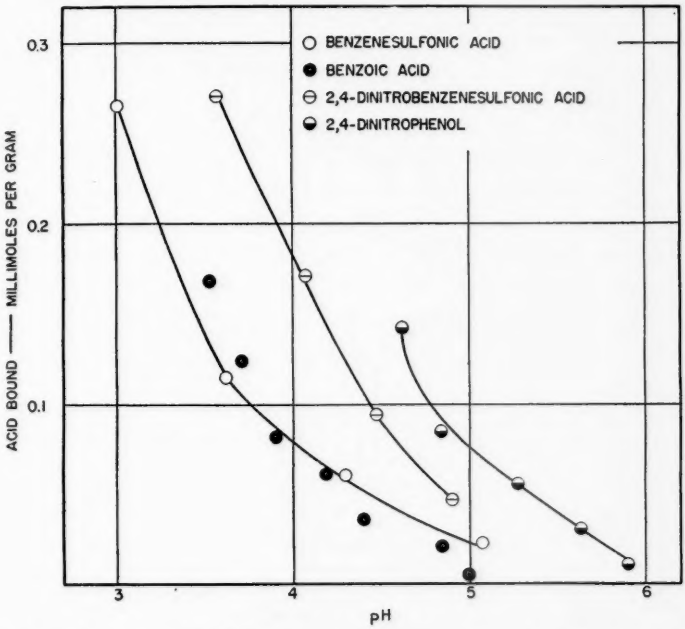

Fig. 8. A Comparison of Portions of the Acid Titration Curves of Wool Protein Obtained with Pairs of Analogous Acids Which Differ Widely in Strength.

sociated analogue, dinitrobenzenesulfonic acid. The opposite situation is found in experiments (still in progress) on a series of aliphatic carboxylic acids. These have even lower affinities for wool than has hydrochloric acid; in addition, the weaker acids have lower affinities than the relatively strong members of the series. The affinities of all of them are increased by the introduction of a halogen or of a hydroxyl group, although the derivatives thus formed are considerably stronger acids. Since there is no consistency in these results it seems likely that the differences found are due to specific structural effects rather than to differences in acidity.

An indication of the nature of the *undirected* forces to which the principal recourse must therefore be had is to be found in the fairly regular correspondence between the order of affinities and of molecular weights, shown in Table 2. Such a dependence on the mass of the anion is consistent with the Fajans rule which deals with the degree of ionic character of bonds, and their consequent tendency to dissociate. However, a dependence on mass, or functions of ion size related to it, is also generally characteristic of similar phenomena which depend, at least in part, on van der Waal's forces, or adsorption.[19]

The several exceptions to a strict correspondence between the relative masses of the ions and their affinities provide further information as to the relation between structure and affinity. Thus the affinities of the aliphatic carboxylates already mentioned do not fall into a molecular weight order; likewise, ethylsulfate ion has as low an affinity as the much smaller chloride ion, and is lower in relative affinity than the smaller bromide and nitrate ions. The anion of trinitroresorcinol is slightly lower in affinity than picrate although it is slightly heavier. Naphthalenesulfonate is higher in affinity than the heavier dinitrobenzenesulfonate ion.

A possible way of resolving these discrepancies without introducing a host of special assumptions is suggested if due regard is had for the shapes of the various ions, and the character of the surfaces which they present to the protein. Two-dimensional ions (those derived from simple benzenoid compounds) appear to possess higher affinities than either compact three dimensional or chain-like particles of the same mass. The nature of the substituents added appears to be of less importance than their mass as long as there is no steric hindrance to their lying in the plane of the ring. Such a hindrance appears to operate in the case of the monovalent trinitroresorcinol ion which has an appreciably lower affinity than picrate. It appears doubtful, from the study of models, whether the undissociated hydroxyl group in this ion can lie in the plane of the ring. When the flat configuration is imposed by the existence of conjugated double bonds, as in naphthalenesulfonic acid, the affinity relative to a disubstituted benzenoid compound of the same mass gains accordingly. Wide differences between the degree of substantivity of *o*- and *m*-substituted benzidine azo-dyes cited by Robinson and Mills[27] furnish extreme examples which are entirely consistent with the present suggestion.

The fact that ion-flatness appears to favor affinity for protein need not be interpreted as an exclusive dependence of affinity on the size of the surface presented by an ion. Saturated aliphatic hydrocarbon chains in an ion probably do not exercise any considerable attractive forces on the fragments of hydrocarbon chains which exist on the surface of the protein. A close approach between them is obstructed by the outer shell of hydrogen atoms common to both. Thus, the greater affinity of ions composed of aromatic hydrocarbons may be due to the absence of this obstructive shell on two of their largest surfaces. If, in addition, electro-negative substituents, such as chlorine, or the oxygen of nitro groups, are presented by the ion to the protein, strong attractive forces may arise, replacing the relative indifference which determines the behavior toward protein of the unsubstituted hydrocarbon. Experiments designed to test these views, and the possibility of applying them in the deliberate control of affinity, are at present in progress.

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Electrophoretic Studies of Nylon

By MILTON HARRIS and ARNOLD M. SOOKNE

A Textile Foundation Publication

Abstract

The surface electrical properties of "unoriented" and of highly "oriented" nylon fibers were investigated by a microelectrophoretic technique. Both types of fibers exhibited definite reversals of charge but at different pH values; the unoriented fiber at pH 3.9 and the oriented at pH 2.7. Since nylon consists of hydrocarbon chains linked together by amide groups, it appears that reversal of charge is principally dependent on the presence of the amide groups, especially since hydrocarbons do not exhibit reversal of sign of charge under comparable conditions. This suggests that amide groups may also influence the electrophoretic behavior of other substances, such as proteins. The difference in the electrophoretic behavior of the two types of nylon is attributed to the difference in their degrees of "crystallinity."

I. Introduction

THE development of new synthetic textile fibers frequently makes it necessary to alter common practices in the textile industry. Thus, new fibers may require new types of scouring, dyeing, or finishing agents depending on the nature of the material. A well-known example of this was the necessity of developing entirely new types of dyestuffs to dye cellulose acetate fibers. That the development of nylon has also presented new problems is not surprising since the chemical and physical properties of this fiber are very different from those of any of the other textile fibers. A number of these problems, such as those involving finishing treatments, are dependent in part on the nature of the surface of the fibers, and more especially on their surface electrical properties. Accordingly, an investigation was undertaken of the surface electrical properties of nylon by the micro-electrophoretic technique as previously used in this laboratory for studying similar characteristics of wool,[1] cotton,[2] and silk fibers.[3]

In addition to these considerations, it appeared that such an investigation might be of value in the general problem of interpretation of electrophoretic data of protein materials. While it has long been recognized that the net charge of proteins under ordinary conditions depends primarily on the degree of ionization of acidic and basic groups (the content of COO^- and NH^+_3 groups) it has more recently been recognized that other groups may play a part as well.[4] Of such groups, the amide groups are present to a large extent in both the proteins and nylon. In the latter, however, they are practically the only polar groups and their role should be more readily

interpretable than in the proteins, where many different polar groups are present.

II. Materials and Methods

Two types of materials were used. One consisted of the so-called "undrawn" or "unoriented" fibers which are obtained by extruding the molten polyamide from a spinneret. The second type of material was the "drawn" or "oriented" fibers obtained by stretching the unoriented fibers approximately four-fold in length.

Both of these materials were extracted with ether to remove surface greases. The method of reducing fibers to a convenient particle size for electrophoretic measurements, the preparation of the suspensions, and the method of measuring the electric mobilities of the suspended particles have been described elsewhere.[1, 2, 3]

All measurements were made in buffer solutions of 0.02 *M* ionic strength. In the pH range between 2.0 and 2.8, hydrochloric acid-potassium chloride solutions were used. Above pH 2.8, acetic acid-sodium acetate buffers were used.

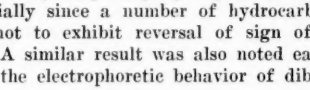
III. Experiments and Discussion

Figure 1 shows the mobility as a function of pH for samples of the oriented and unoriented nylon fibers. The oriented nylon exhibits a reversal of sign of charge at about pH 2.7 and the unoriented material at about pH 3.9.

Nylon is a polyamide prepared by the interaction of a diamine and a dicarboxylic acid and has the following type of structure:

$$-CO-R-CO-NH-R'-NH-CO-R-CO-NH-R'-NH$$

where R and R′ may represent 4 and 6 methylene ($-CH_2-$) groups. Chemically, therefore, nylon consists principally of hydrocarbon chains linked together by amide groups. Presumably the ends of the chains may contain free basic or acidic groups but the presence of such groups in a polymer of this type may be very difficult to detect.[5] Regardless of this, however, the proportion of these groups which may be expected to be free in the nylon polymer is extremely small and should not appreciably influence the behavior of the material. It appears, then, that the reversal of sign of charge may be principally dependent on the presence of the amide groups, especially since a number of hydrocarbons already studied[6] have been shown not to exhibit reversal of sign of charge under comparable conditions.* A similar result was also noted earlier in this laboratory[7] in investigating the electrophoretic behavior of dibenzyldiketopiperazine,



This substance, which is not amphoteric in the usual sense (in that it contains no free carboxyl or amino groups) but contains two amide groups,

* The sign of charge of these substances can undoubtedly be reversed in solutions of much lower pH than are used in this work and then are generally used in similar investigations on proteins. It should also be noted that substances which do not show reversals of sign of charge in the presence of uni-univalent salts frequently do so when polyvalent ions are present.

exhibited a definite reversal of charge at pH 2.9. Thus the possible influence of the amide groups on the electrophoretic behavior of some substances such as proteins must be given consideration, although such influence may be obscured when large numbers of acidic and basic groups are present.

That different pH-mobility curves and different isoelectric points were obtained for the oriented and unoriented nylons is of considerable interest although it was not unexpected. Similar differences have been noted for the electrophoretic properties of other substances when studied in both the amorphous and crystalline states. Earlier work by Wintersteiner and

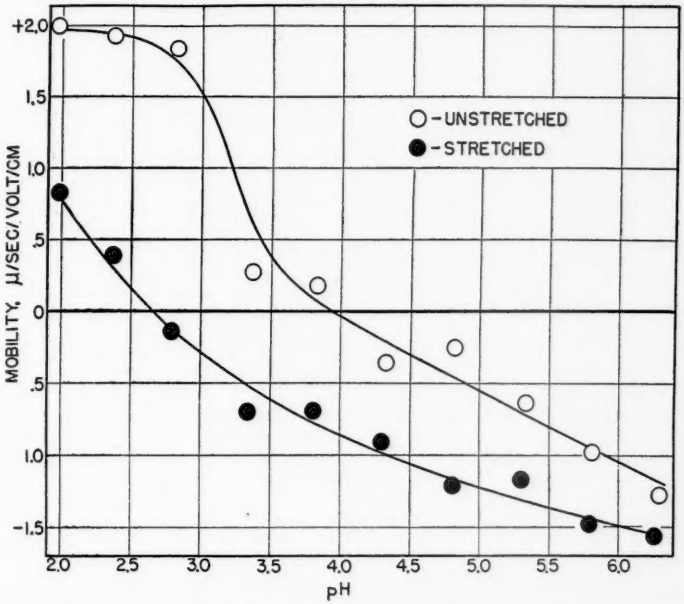


Fig. 1. pH-mobility Curves for Stretched and Unstretched Nylon.

Abramson [3] showed that the isoelectric point of amorphous insulin was at pH 5.35 while that of insulin crystals was found at pH 5.0.* It was further shown by Abramson and Moyer [4] that the isoelectric points of various amino acid crystals all occur at pH values below the values found for the amorphous or dissolved substances. While it has not been common practice to consider fibers crystalline in this same sense, nevertheless the X-ray diffraction patterns do indicate a far more orderly or "crystalline" arrangement in the oriented nylon as shown in figure 2. Stretching the unoriented nylon probably produces a fairly parallel arrangement of the long chain mole-

* It was not known in this case how much adsorbed insulin was on the surface of the crystalline insulin. The difference might have been greater if no dissolved insulin had been present.

cules. Such a process tends towards a maximum of interaction between the molecules, and thus changes the character of the surface. This would be expected to alter the electrophoretic mobility of the substance. On the basis of these considerations, it may be concluded that the difference in the electrophoretic behavior of the two types of nylon used in this investigation is related to the difference in their degrees of "crystallinity."*

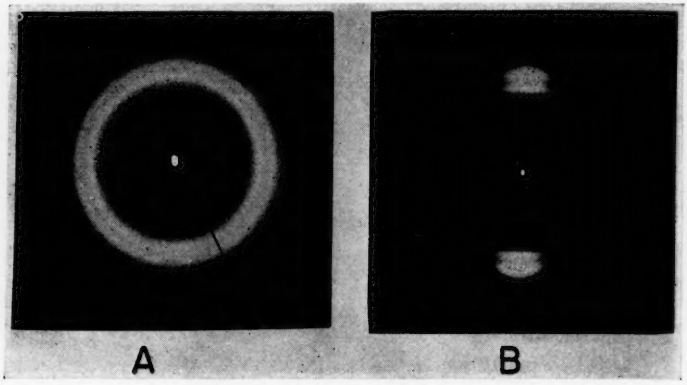


Fig. 2. X-ray Diffraction Patterns of Nylon. A, Unstretched; B, Stretched.

Acknowledgment

Thanks are due Dr. J. B. Miles of the Du Pont Company for furnishing the samples of nylon and the X-ray diffraction patterns.

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*A similar phnomenon was recently reported by Kanamaru and Takada [9] who found that the ζ-potential of viscose varies with the velocity at which the fibers were originally spun; i.e., with their degree of parallelism.

Abstract of Papers Presented before the Division of Cellulose Chemistry American Chemical Society*

The Action of Light on Cellulose. VI. A Method for the Measurement of the Osmotic Pressure of Colloidal Solutions.

By RALPH E. MONTONNA and L. T. JILK.†

In studying the action of light on cellulose and its derivatives, it was desirable to have a rapid and accurate method of measuring the average particle size which was independent of solvation and could be carried out in organic solvents at room temperatures. The static methods were too slow and at high pressures in organic solvents resulted in injury to the membranes. By suitable modification of the apparatus designed by van Campen for the dynamic method of Berkeley and Hartley, accurate and rapid determinations of the particle weight of colloidal dispersoids could be attained. The apparatus is described in detail and the method of use in this type of measurement. For acetone solutions of cellulose derivatives, denitrated collodion membranes prepared according to a definite standard procedure proved quite satisfactory. The method of preparation of these mebranes is described.

Mesylated Cellulose and Derivatives.

By M. L. WOLFROM, J. C. SOWDEN, and E. A. METCALF.‡

Mercerized cotton linters (or regenerated cellulose from cellulose acetate) in pyridine suspension reacts heterogeneously and slowly with methanesulfonyl chloride (mesyl chloride) at room temperature. After forty-eight hours 1.8 mesyl groups per glucose unit can be introduced, the product containing no nitrogen and only a trace of chlorine. A quantitative study of the rate of introduction of sulfur showed no break in the curve corresponding to initial primary alcohol substitution. Longer periods of time resulted in a slow decrease in mesyl content, probably due to reaction with pyridine hydrochloride.

A cellulose acetate containing 1.7 acetate groups per glucose unit was mesylated as above and a product obtained that contained 1.0 mesyl group per glucose unit, no nitrogen, and only a trace of chlorine. Treatment of

* St. Louis, Missouri, April 7–11, 1941.
† University of Minnesota, Minneapolis, Minn.
‡ The Ohio State University, Columbus, Ohio.

this product with pyridine and pyridine hydrochloride at 80° lowered the mesyl content and introduced chlorine.

The above mixed mesyl cellulose acetate (1.7 acetate and 1.0 mesyl groups per glucose unit) reacts with sodium iodide in acetonylacetone to yield products that are sulfur-free but contain only 0.4 atom of iodine per glucose unit (18% iodine). The action of aqueous ammonia on mesyl cellulose or the above mesyl cellulose acetate, under various conditions, led to partial replacement of the mesyl groups to produce products that contained appreciable amounts of sulfur (3 to 6%) and nitrogen (0.5 to 4%).

Mixed Acetate *o*-Pentaacetylgluconate Esters of Cellulose.

By M. L. WOLFROM and P. W. MORGAN.*

Cellulose acetate (1.7 acetate groups per glucose unit) was reacted with gluconyl chloride pentaacetate (a) in pyridine solution, to yield a product containing 0.7 *o*-pentaacetylgluconate group per glucose unit and (b) in a chloroform solution of triethylamine, to yield a product containing 0.3 *o*-pentaacetylgluconate group per glucose unit. In preliminary experiments on the esterification of polyhydric compounds with gluconyl chloride pentaacetate in pyridine solution, a crystalline di-ester of ethylene glycol was obtained and amorphous, fully esterified derivatives of glycerol, mannitol and alphamethylglucopyranoside were formed.

Shrinkage and Cell Wall Structure of Cotton Fibers.

By EARL E. BERKLEY.†

In order to obtain a better understanding of the structure of cotton fibers in the range between the particle size observable in the microscope and that measurable by means of x-ray technique, a study of shrinkage was undertaken. Green cotton fibers between the ages of 10 and 28 days were dropped into boiling water for 5 to 10 minutes and then used immediately or preserved in about 70 per cent alcohol until used. Longitudinal shrinkage of these fibers when dried showed a gradual decrease from the tenth day until secondary thickening began. The shrinkage decreased rapidly for the following two to five days, after which little change was noted. The per cent shrinkage was increased by extracting the fiber with hot 95 per cent alcohol to remove the waxes and further increased by extractions with certain solvents to remove the pectic substances. A large percentage of the primary wall appeared to dissolve in hot sodium hydroxide.

The results show that in the primary wall the crystalline cellulose lies with its major axis transverse to that of the fiber. They further indicate that a large percentage of the primary wall is amorphous material, presumably cellulose in which the fine crystals of cellulose are dispersed. The removal of waxes and pectins from the cellulose matrix appears to leave voids which collapse upon drying.

* The Ohio State University, Columbus, Ohio.
† Bureau of Plant Industry and Agricultural Marketing Service, U. S. Department of Agriculture.

The Hydrolysis and Catalytic Oxidation of Cellulosic Materials. III. The Rates of Hydrolysis of Cotton Mercerized with and without Tension.

By R. F. NICKERSON.*

The effects of mercerization with sodium hydroxide on the behavior of cottons toward an aqueous acid-catalyst mixture are examined. This new method depends upon the digestion of cellulose in hydrochloric acid-ferric chloride reagent; the glucose set free by hydrolysis is rapidly oxidized. The evolved carbon dioxide, determined periodically during a 7-hour run, is convertible to percentages of cellulose broken down.

The data indicate that both mercerized and unmercerized cottons consist of two structural components, one of which splits out during hydrolysis, and an acid-resistant residue which probably represents crystallites. Mercerization increases the proportion of accessible or amorphous cellulose. From a consideration of the augmented physical properties and chemical reactivity which accompanies the increased amorphousness, the conclusion is reached, in agreement with other investigators, that many of the characteristics of cellulose are intimately related to the amounts of crystalline and amorphous components. The method appears to be suitable for determining the distribution between the latter states.

Estimation of Reducing Groups in Cellulosic Materials.

By MILTON HARRIS, A. R. MARTIN, and LEONARD SMITH.†

The reducing groups in cellulosic materials may be readily estimated by a modification of the method of Bergmann and Machemer. Investigation of the rates of oxidation by iodine of a series of hydrocelluloses at 0° C. and pH 10.6 showed that there is an initial rapid reaction with iodine during the first hour, followed by a secondary reaction during which iodine is consumed at a very much slower but practically constant rate. Standard A.C.S. cellulose (cotton) shows only a very slight initial reaction with iodine, but after approximately 1 hour exhibits a secondary reaction of the same rate as the hydrocelluloses. By applying a correction for the amount of iodine consumed in the secondary reaction, it is possible to estimate the iodine utilized in the oxidation of reducing groups. Since iodine utilized in this way apparently oxidizes aldehydic to carboxylic groups, an independent check is readily obtained by estimation of the carboxyl groups thus formed by titration with silver *o*-nitrophenolate.

The amount of iodine absorbed by the degraded cellulose allows one to follow quantitatively the mechanism of the hydrolysis. Freundenberg, Kuhn, et al., have investigated kinetically the hydrolysis of cellulose with sulfuric acid at high degrees of cleavage and have focused their attention on low molecular weight cleavage products, such as cellotriose, cellobiose, and biosan. The improved experimental accuracy of the iodine method has permitted the extension of this kinetic study into the truly high polymeric field of the hydrocelluloses. Our experiments give rate constants of the

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† Research Laboratory of The Textile Foundation, National Bureau of Standards, Washington.

order 10^{-4} in reasonable agreement with the constants of Freundenberg, Kuhn, et al.

The Oxidation of Cellulose by Nitrogen Dioxide.

By E. C. YACKEL and W. O. KENYON.*

Cellulose has been oxidized by means of nitrogen dioxide to produce a series of oxidized celluloses of various carboxyl group contents. Even at high degrees of oxidation the products retain a fibrous structure. Procedures for analyzing these materials by the calcium acetate and the CO_2 evolution method and the results obtained are given. Above a carboxyl group content of about 13%, these oxidized celluloses dissolve quickly and completely in 2% aqueous alkali at room temperature. The properties of this type of oxidized cellulose and of its salts are described and discussed.

Investigation of the Properties of Cellulose Oxidized by Nitrogen Dioxide. I.

By C. C. UNRUH and W. O. KENYON.

A series of oxidized celluloses of combined carboxyl group contents from 5.8 to 25.3%, prepared by the action of NO_2 on cellulose, were analyzed for carboxyl by several methods. The results indicate that the carboxyl groups are present as uronic acid. Acetylation data and furfuraldehyde evolution are in agreement with these results. The products appear to consist of anhydro glucose units and anhydro glucuronic acid units.

Formation of Cellulose Crystallites in Plastids of Living Plant Cells.

By WANDA K. FARR.†

The formation of sugar from inorganic substances takes place in the chloroplasts of living plant cells. A chloroplast is a distinct organic structure separated from the other protoplasmic contents by a membrane. When the amount of sugar produced becomes excessive, it is converted, within the chloroplast, into starch in the form of crystalline grains.

Through the activity of living protoplasm, sugar is also converted into crystalline granules of cellulose. When these cellulose particles were identified in living protoplasm in 1934, no clue was obtained as to a particular organic structure in which this conversion takes place. Cellulose-forming chloroplasts and colorless plastids are now identified in which the operation of a process contributing uniformity in size and shape to the cellulose crystallites is clearly visible.

The cellulose particles embedded in the plastid plasma are freed into the protoplasm by the rupture of the plastid membrane. In the cell wall the cellulose particles constitute the crystalline phase and the plastid plasma, often including even the chlorophyll, is represented in the intercrystalline phase. These observations extend the information as to certain physical aspects of cellulose formation and confirm our earlier conclusions as to the formation and structure of the cell wall.

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† American Cyanamid Co., Stamford, Conn.

Abstracts

Committee on Abstracts and Bibliography:
E. R. Schwarz, Chm., Dr. E. J. Saxl, C. H. Clark.

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I. Fibers (Synthetic and Natural) and Fiber Analysis

The Amorphous Structure of Cellulose and Its Derivatives. V. A. Kargin and P. V. Kozloff. *Kino Photo Chem. Ind.* (*U.S.S.R.*), 1940, No. 4, P. 40–6; abs. in *Eastman Kodak Abs. Bull.*, October 1940, P. 538.

Various theories concerning the structure of cellulose and its derivatives are briefly reviewed. On the basis of x-ray and electron diffraction studies, it is concluded that the equilibrium state of cellulose is an amorphous structure and that structures approaching the crystalline state are unstable, tending towards the amorphous state. The most favorable state is described as an oriented state in which the chains as a whole are oriented, the individual chains being curved rather than straight. (S)

Cellulose: Swelling, Alkali, Adsorption and Solubility in Alkali. G. Saito. *J. Soc. Chem. Ind., Japan*, 1940, V. 43, P. 160B–61B; abs. in *J. T. I.*, November, V. 31, P. A621.

Curves are given showing the effects of dilution of the caustic soda solution and of change in temperature on the swelling and the apparent alkali adsorption of ramie and cotton in caustic soda solutions. At 20° C. dilution of the alkali causes decreases in alkali adsorption whilst the swelling increases, passes through a maximum and then decreases. The changes are dependent on the original concentration of alkali. Observations of X-ray diagrams on dilution of Na-Cellulose II and Na-Cellulose I show that

the diagrams do not change until concentrations corresponding to the swelling maxima are reached. Swelling and alkali adsorption increase with reduction in temperature, but increase in temperature produces very little decrease in swelling and alkali adsorption. Curves showing changes in degree of swelling and solubility of ramie and rayon fibers with changes in alkali concentration show a parallelism in the variations of these two properties. At 0° C. the concentration of alkali producing maximum swelling is lower than that at 20° C. The higher the degree of swelling at which a part of the cellulose is dissolved, the higher is the viscosity of the dissolved constituent. It is thus possible to fractionate high molecular substances by stepwise increases of swelling. (C)

CHEMICAL AND PHYSICAL CHANGES IN VEGETABLE FIBERS PROCESSED TO RESEMBLE COTTON. Ernesto Afferni. *Ann. chim. applicata*, V. 30, P. 3–10 (1940); abs. in *C. A.*, V. 34, Col. 6819.

The chem. changes in hemp processed into staple-like cotton "cafioc" are investigated. All the lignin in hemp is extd. during the process, the moisture content increases from 6.2 to 8.5%, while the ash drops from 1.15 to 0.60%. The β-cellulose disappears, while α-cellulose increases from 81.50 to 88.93%. The pentosans in hemp are almost entirely removed by the alk. treatment. The affinity for dyes is also improved. (C)

COTTON, CUPRAMMONIUM RAYON AND RAMIE FIBER: ABSORPTION OF ALKALI, AND SWELLING. G. Saito. *J. Soc. Chem. Ind., Japan*, 1940, V. 43, P. 133–36B; abs. in *J. T. I.*, November, V. 31, P. A621.

The cellulose-alkali system has been studied by steeping the fiber in the alkali hydroxide solution containing salt and determining the change in the composition of the supernatant liquid. In the absence of definite information about the fixation of salt by cellulose, the method leads to lower limits for the amount of alkali and water taken up. Values (Mol. per $C_6H_{10}O_5$) of the apparent absorption of alkali hydroxide and these lower limits for water and alkali, as well as values of the cross-sectional swelling, are plotted as functions of equilibrium concentration for cuprammonium rayon, ramie and cotton in Na, K and Li hydroxide at 20° C. At the same alkali concentration the alkali absorption decreases in the order rayon, ramie, cotton. The curves for water fixation by ramie suggest that Li, Na and K hydroxides give hydrates with, respectively, 7, 6 and 3 H_2O per $C_6H_{10}O_5$. (C)

COTTON AND RAYON FIBERS: STRUCTURE. *Text. Mercury and Argus*, 1940, V. 103, P. 106–107; abs. in *J. T. I.*, Oct. 1940, V. 31, P. A566.

The writer briefly reviews Miss Farr's conception of the structure of cellulosic fibers and recent papers by Miss Clegg (B.C.I.R.A.) and by Hock and Harris that provide evidence for the older micelle theory. He suggests that there may be a parallel between the facts (1) that a small residuum of pectin in cotton so strongly restricts dissolution of the fiber in cuprammonium and (2) that a small amount of regenerated cellulose produced in cellulose acetate filaments by saponification so greatly reduces the solubility of the acetate in acetone or acetic acid. (C)

DU PONT ANNOUNCES "FIBER D." Herbert R. Mauersberger. *Rayon Text. Mo.*, Jan. 1941, V. 22, P. 38–9.

A new viscose staple fiber of permanent crimp, rounded smooth cross-section, and high covering power that imitates wool closely. (C)

II. YARNS AND FABRICS

COLD PROCESS WEIGHTING OF COTTON PIECE GOODS. H. L. Miller. *Rayon Text. Mo.*, Jan. 1941, V. 22, P. 66–7. (C)

FINISHING UNSHRINKABLE COTTON FABRICS. *Canadian Text. J.*, 1940, V. 57, No. 20, P. 34–5.

Final washing, drying and tentering operations to finish cotton goods with less than 1% shrinkage, without the use of specialized equipment. (C)

FLAX AND HEMP SANDBAG FABRICS: ROTTING. *Jute Review*, 1940, V. 13, 5, P. 13, 6, P. 13; *Rev. Appl. Mycol.*, 1940, V. 19, P. 538–39; abs. in *J. T. I.*, November, V. 31, P. A624.

In connection with Barker's investigations on the reaction of processed jute to fungal infection, some figures recently published by the German Fibre Research Institute relating to similar tests on flax and hemp are reproduced. Samples of sandbag fabrics made from flax and hemp tow yarns were (1) exposed to day and night weathering for six months at different places. Others were (2) stored in moist sand at 20° C. and a further lot (3) in an atmosphere of 80 to 90%, relative humidity and a temperature of 18° to 20°, part of each lot being impregnated with copper sulphate and part left untreated. In lot (1) the first signs of mould appeared after one month and gradually increased until considerable infection was present at the end of six months. In (2) the untreated samples were covered with fungi after one month and completely destroyed at the end of three months, whilst the impregnated, though severely attacked after three months, still showed adequate strength. As regards (3) the controls were heavily moulded after three months, whilst the treated samples remained free for six months. There was no difference between flax and hemp in respect of resistance to fungal invasion, but the latter gave higher values than the former in bursting tests. (C)

HIGH-SPEED PHOTOGRAPHY AND THE STUDY OF RAPID MACHINE MOTIONS. V. Sepavich and A. Palmer. *Mech. Engineering*, July 1940, V. 62, P. 519–24; abs. in *Eastman Kodak Abs. Bull.*, December 1940, P. 620.

The application of the Edgerton lamp and stroboscope to the photographic study of the motion of certain high-speed machine parts, namely, the loom shuttle, is discussed briefly. This work was done before the introduction of the Kodatron Speedlamp. (S)

JUTE SANDBAG FABRICS: DETERIORATION IN SOIL. S. G. Barker. *Jute Review*, 1940, V. 13, 139, P. 5, 140, P. 5; *Rev. Appl. Mycol.*, 1940, V. 19, P. 538; abs. in *J. T. I.*, Nov., V. 31, P. A623.

In one test the periods (in days) of soil exposure required for the complete breakdown of jute samples shielded by glass, aluminium, rubber and vaseline were 119, 105, 105, and 32, respectively, compared with 28 for the untreated. In active garden soil, dew- and water-retted flax, hemp,

jute and cotton decayed in 20, 20, 21, 35 and 14 days, respectively, the rate of deterioration being roughly inversely proportional to the weights of the fabrics (4.42, 4.42, 4.42, 7.47, and 1.78 g. per 100 sq. cm., respectively). It is thus apparent that jute is superior, from the point of view of resistance to rotting, to most of the other possible materials, besides being cheaper. In another experiment in which jute wool sheets were exposed to the action of soil, the strongest protective influence was exercised by acetylation: this process conferred immunity from the complex of microbiological agents co-operating with climatic conditions to induce deterioration for a period of 2,645 days compared with 45 for the untreated control samples, a ratio of 58.8: 1. Good results were also given by chromium/cutch, proflavine, acriflavine, and copper naphthenate with protective prolongation ratios of 2.4: 1 for the first three and 2.2: 1 for the fourth. Resistance to sea water (tested in a few instances only) was strengthened by treatment with copper oleate (2.8: 1) and shielding with latex (2.1: 1). (C)

MODERN MERCERIZING. PART IX. THE ACTION OF NaOH. Lewis Thompson. *Text. Recdr.*, 1940, V. 61, No. 690, P. 35–6; *ibid.*, V. 60, No. 689, P. 28, 31; V. 59, No. 688, P. 31–2, 34; V. 58, No. 687, P. 29, 31–2; V. 57, No. 686, P. 28–29; V. 57, No. 685, P. 31–3; V. 57, No. 684, P. 31, 33, 35; V. 57, No. 683, P. 31–3; V. 57, No. 682, P. 33–5.

This instalment consists of a very brief review of the work on the preferential absorption of NaOH and the possibility of compound formation between cellulose and sodium hydroxide. (C)

PEBBLE IN CREPE. George Thomas. *Text. Wld.*, Jan. 1941, V. 91, P. 80.

Effect of various soaking ingredients is discussed. Fabric moulage provides durable record and its making is described. (C)

PHOTO-ELECTRIC SIDE REGISTER CONTROL. H. E. Overacker. *Rayon Text. Mo.*, Nov. 1940, V. 21, P. 68–70. (C)

THE STORAGE OF RAYON AND ITS PRETREATMENT FOR FUTURE PROCESSING OPERATIONS. Albert Schulze. *Deut. Wollen-Gewerbe*, V. 72, P. 312 (1940); *Chem. Zentr.*, 1940, I, 3601; cf. *C. A.*, V. 33, 7578; *Ibid.*, V. 34, Col. 6085.

For storage, rayon should have a permanent moisture content of 11%. The crushing of threads, etc., in storage should be avoided. Instead of paraffin it is better to use oils that are removed readily by rinsing. (C)

STREAKINESS IN SYNTHETIC FABRICS. J. J. Sussmuth. *Rayon Text. Mo.*, 1940, Sept., V. 21, P. 80–2; Oct., V. 21, P. 53–4; Dec., V. 21, P. 67–8; 1941, Jan., V. 22, P. 63. (C)

TEXTILE DRYING. Fred Kershaw. *Rayon Text. Mo.*, 1941, Jan., V. 22, P. 68–9; Feb., V. 22, P. 63–5. (C)

TEXTILE MODERNIZATION FOR DEFENSE. *Text. Wld.*, Nov. 1940, V. 90, P. 91–114.

The Editors indicate in a series of articles just what constitutes maximum efficiency in all phases of their activity. Not only in plant, equip-

ment, engineering facilities and supplies—but in employer-employee relationships, working conditions, protection against sabotage, production, planning, merchandising, purchasing, and the many other functions of management. (C)

III. Chemical and Other Processing (Not Otherwise Classified)

Nitrogenous Compounds Used in Textile Treatments. L. Bonnet. *Rev. Gén. Mat. Col.*, 1940, V. 44, P. 168–172 (through *Brit. Chem. Abs. B.*, 1940, V. 59, P. 598); abs. in *J. T. I., Oct.* 1940, V. 31, P. A560.

The uses of many nitrogenous textile auxiliary products including the Sapamines, Solidogens, Fixanol, Velan PF, etc., are discussed, the structure and action of the various types being given. Work carried out on the colloid chemistry of surface-active agents is reviewed. (C)

Photographic Printing on Cloth. M. Makover. *Soviet Foto*, 1938, No. 15, P. 36; abs. in *Eastman Kodak Abs. Bull.*, November 1940, P. 566.

The method, which is practically the same as that described in the succeeding abstract, is simple and may be done without special equipment. White or colored cloth is immersed in a 3% filtered salt solution, pressed out almost dry, stretched in a frame, and brushed with an 8% solution of silver nitrate. This operation may be carried out in red light, while the cloth is dried in the dark. The cloth is then exposed to daylight or artificial light under a negative. The sensitivity is approximately the same as that of daylight paper or blueprint paper. The correct exposure is determined by experiment. Two methods may be used: The cloth is either (1) fixed in a 20% solution of hypo or (2) immersed in the following developing solution: Water, 1000 cc.; sodium sulfite (crystal), 80 gm.; sodium carbonate (crystal), 80 gm.; and para-aminophenol, 4 gm. After development, the cloth is fixed in the usual manner. A brush may be used for development and fixing. The developing image may be colored either immediately or some time later, since the image keeps well. The choice of the color depends upon the tone of the cloth and should be in harmony with the latter. The image is first bleached in the following solution: Lead nitrate (10% solution), 15 cc.; potassium ferricyanide (10%), 10 cc.; and water, 75 cc., washed in weak nitric acid (1: 1000), and washed with two or three changes of water for 3 to 4 minutes in each change. After this treatment, the cloth may be toned either blue, green, red, or violet, using the following toning solutions: *Blue.* Ferric alum (10% solution), 20 cc.; potassium bromide (10%), 12 cc.; nitric acid (10%), 1 cc.; and water, 70 cc. *Green.* Ferric alum (10%), 10 cc.; potassium bromide (10%), 5 cc.; potassium bichromate (saturated solution), 5 cc.; and water, 100 cc. *Red.* Copper sulfate (10%), 50 cc.; silver nitrate (10%), 3 cc.; and water, 50 cc. *Violet.* Copper sulfate (10%), 30 cc.; ammonium acetate (10%), 20 cc.; and water, 50 cc. The colors may be brightened in a 10% hypo solution. (S)

The Practical Art of Color Matching. William H. Peacock. *Rayon Text. Mo.*, 1940, October, V. 21, P. 61; Nov., V. 21, P. 63–7; Dec., V. 21, P. 72–4; 1941, Jan., V. 22, P. 72–5; Feb., V. 22, P. 66–8. (C)

PROGRESS IN MERCERIZATION. Chas. F. Goldthwait. *Text. Wld.*, October 1940, V. 90, P. 82–3.

On 50th Anniversary of Lowe's patent trend is to higher speed, better control. (C)

SOME NEW DYEING AND FINISHING AUXILIARIES CONTAINING NITROGEN GREASE AND WATER REPELLENTS. J. Wakelin. *Silk & Rayon*, September 1939, V. 13, P. 740–2. (C)

STAPLE FIBRE MUSLIN: DYEING WITH NAPHTOL AS DYES AND DISCHARGE PRINTING. F. Streng. *Textilber.*, 1940, V. 21, P. 180–82; abs. in *J. T. I.*, July 1940, V. 31, P. A386.

Difficulties encountered in the dyeing of staple fibre materials with Naphtol AS dyes, especially in processes involving the use of Variamine blue diazo solutions, and particularly in dyeing for subsequent discharge printing and in the production of reserve prints, are discussed and methods of overcoming them are explained. Modifications of the procedures used for cotton goods and various precautions necessary in the dyeing and printing operations are described. Suitable vat dyes for the production of various colored discharges are mentioned. (C)

STAPLE FIBRE AND STAPLE FIBRE-WOOL FABRICS: SIMULTANEOUS DESIZING, WASHING AND DYEING. F. Jahnes. *Tetilber.*, 1940, V. 21, P. 182–83; abs. in *J. T. I.*, July 1940, V. 31, P. A382.

When staple fibre and staple fibre-wool mixture fabrics are to be dyed with substantive, diazo or half-wool fast dyes in shades for which a preliminary bleaching is not necessary, desizing, washing and dyeing can be effected simultaneously by using dyeing baths containing Biolase, Laventin BL and Igepon T. Recipes and details of suitable procedures are given. Clear level shades are obtained and the goods have a full, soft handle. (C)

TEXTILE APPLICATIONS OF THE PHOSPHATES: LAUNDRY USES FOR TRISODIUM PHOSPHATE. G. S. Ranshaw. *Chem. Age* (London), V. 41, P. 299–300 (1939); abs. in *C. A.*, V. 34, Col. 3924 (1940).

The use of Na_3PO_4 in bleaching and in wool washing is discussed. Na pyrophosphate is a "stabilizer" for H_2O_2 in bleaching, permitting regular evolution of O. (C)

VELOCITY OF DYE ABSORPTION OF GERMAN STAPLE RAYONS. H. A. Wannow and K. Stephany. *Mell. Textilber.*, 1939, V. 20, P. 710–12; abs. in *C. A.*, 1940, V. 34, Col. 3500.

The comparative dyeing velocities of 6 com. German rayons were measured by use of representative members of the oxazine, S, developed and vat series of dyestuffs. Significant differences were noted in every case. Cuprama SK, presumably a Cu-ammonia process rayon, took up dyes much more rapidly than the other samples. To obtain level dyeings on mixts. of various rayons the individual components should have dyeing velocities of about the same order. (C)

WOOL DYEING AT ATMOSPHERIC TEMPERATURE. J. M. Gaudit. *Teintex*, 1940, V. 5, P. 183–85; abs. in *J. T. I.*, July 1940, V. 31, P. A386; *C. A.*, V. 34, Col. 6080.

Animal fibres may be dyed in a cold bath containing a proportion of acid varying according to the depth of shade desired. Tests were made

with lactic, acetic, formic and sulphuric acids. Formic acid gave the most satisfactory exhaustion. (C)

IV. Research Methods and Apparatus

Examination of the Degradation Products of Cellulose. Robert Garin. *Rusta-Rayonne*, V. 14, P. 485–91 (1939); abs. in *C. A.*, V. 34, Col. 6446.

Phys. modifications of cellulose fibers are compared with degradation products which are prepd. by chem. decompn. of cellulose. Treatment of cellulose by strong acids in presence of H_2O swells fibers and produces a phys. modification of cellulose which is much more reactive to reagents than untreated cellulose. Treatment of cellulose by strong acids and subsequent drying in presence of the acid modifies cellulose chemically, forming hydrocellulose (I), while oxidation by oxidizing agents produces oxycellulose II. The hydrolyzing action converts the alc. groups of cellulose into aldehyde groups while oxidation to (II) produces COOH groups. The following reactions can be applied to these products: Mercerized cotton can be detected in the presence of untreated cotton by subjecting the sample to a soln. of I in KI in the presence of $ZnCl_2$. Mercerized cotton turns brown while untreated cotton remains colorless. I and II reduce Fehling's solns. II gives the "Turnbull's reaction" when treated with Fe salts and subsequently with solns. of $K_3Fe(CN)_6$. The acidic groups of II retain sufficient Fe to produce this reaction. (C)

Fluorescence Microscopy. J. Grant. *The Microscope*, May–June 1940, V. 4, P. 146–55; abs. in *Eastman Kodak Abs. Bull.*, October 1940, P. 524.

An elementary discussion of fluorescence microscopy, with a description of some applications, is given. It is valuable in the examination of paper fibers, both to distinguish the unbleached from the bleached, and by secondary fluorescence, with dyes, to identify the fibers. (S)

The Formation of Images of Transparent Objects in the Microscope. D. S. Rogestwensky. *J. Physics* (*U.S.S.R.*), 1940, V. 2, No. 4, P. 323–46; abs. in *Eastman Kodak Abs. Bull.*, November 1940, P. 583.

An analysis is made of the interference and diffraction effects seen in a microscope when transparent objects are viewed. (S)

Lanital: Determination in Mixtures with Wool and Other Fibers. A. Cappelli and R. Tuffi. *Boll. Assoc. Italiana Chim. Tess. e. Color.*, 1939, V. 15, P. 129–136; abs. in *J. T. I.*, July 1940, V. 31, P. A395.

Difficulties encountered in the determination of Lanital, especially dyed Lanital and stabilized Lanital, in mixtures with wool by the methods hitherto used are discussed and a new method is described that depends on treatment of a sample with a solution containing 20% of sodium sulphide and 2% of sodium hydroxide for 30 min. at 60° C. The wool is dissolved by this treatment. With mixtures containing staple fiber and cotton, these fibers, like the Lanital, remain undissolved. The content of staple fiber or cotton in mixtures with Lanital and wool can be determined from the loss in weight on treatment for 2 hrs. at 18–20° with sulphuric acid of 58 Bé. Results obtained in the analysis of Lanital-wool and Lanital-wool-viscose staple fiber mixture fabrics by the new method and by the method of Cerbaro are tabulated and discussed. (C)

METHODS FOR THE QUANTITATIVE CHEMICAL ANALYSIS OF YARNS AND FABRICS MIXED WITH LANITAL. Giovanni Baroni. *Boll. ufficiale staz. sper. seta*, V. 8, P. 31–40 (Sept. 1938); *Chem. Zentr.*, 19[illegible], I, P. 1283–4; abs. in *C. A.*, 1940, V. 34, Col. 6819.

After a crit. discussion of other methods the meth[illegible] of the R. Stazione Sperimentale per la Seta is described. If the specim[illegible] is a mixt. of wool and lanital alone the procedure is as follows: Treat a [illegible]shed sample, dried at 105–10°, with 10% KOH for 30 min. at 50°, shaki[illegible]e flask each 2 min. and keeping the temp. const. at 50–1°. After exactly 30 min. the wool is completely dissolved while the lanital remains undissolved. Filter, wash, dry and weigh the lanital. Multiply the amt. detd. by the factor 1.08. In the presence of cellulose fibers remove these first by treatment with coned. H_2SO_4 for 30 min. at 30° and det. If acetate silk is simultaneously present, remove it by boiling with acetone and then det. If wool, lanital, rayon and cotton are all present, det. wool and lanital as above in one portion of the sample, while in another portion det. the cotton and rayon after the wool and lanital have been removed by boiling with 10% NaOH for 1 min. and then with 20% NaOH for 10 min. Det. the cotton by the usual methods and the rayon by difference. (C)

NEW METHOD OF DETERMINING THE WETTABILITY OF TEXTILE FABRICS. C. M. Blow and B. F. J. Moxon. *J. Soc. Chem. Ind.*, 1940, V. 59, P. 171–174; abs. in *J. T. I.*, Oct. 1940, V. 31, P. A569; C. A., V. 34, Col. 8289.

A new technique for the determination of the wettability of textile fibers is described. It is carried out on yarn and the wettability figure obtained has been shown to be independent of the count and twist. At present the measurements are confined to one quality of wool, but work of an experimental and theoretical nature is in hand to enable the wettability of fibers of different diameters to be determined and compared. The results given in this paper are chiefly concerned with establishing the principles of the method, but the effects of scouring, dyeing, unshrinkable processes, and "Velan" treatment of wool are examined in a preliminary manner. (C)

A NOTE ON MOISTURE CONTENT AND REGAIN CALCULATION CHARTS. J. Tankard. *J. T. I.*, August 1940, V. 31, P. T201.

Two charts are described and illustrated, by means of which it is possible to obtain, without any mathematical calculation, the value of any one of the quantities x, y or z in expressions of the type

$$\frac{x-y}{x}=z \text{ or } \frac{x-y}{y}=z$$

when the values of the other two quantities are known. Special reference is made to the use of these charts in determinations of the moisture content and/or moisture regain of textile materials. (C)

STAPLE FIBER: TESTING. W. Weltzien. *Monatshefte Seide u. Kunstseide*, 1938, V. 43, P. 388–392, 418–426, 462–471, 505–518; 1939, V. 44, P. 15–18, 52–60, 97–102, 156–162, 191–198, 225–228, 324–330; abs. in *J. T. I.*, Sept. 1940, V. 31, P. A504.

A review of methods for testing staple fiber: the literature is comprehensively surveyed, approved apparatus is described, and data are tabulated. (C)

V. Pure Science, Economics and Misc.

The Mechanism of the Degradation of Cellulose. S. M. Kaji and K. Venkataraman. *Current Sci.*, V. 9, 66–7 (1940); abs. in *C. A.*, V. 34, Col. 5655.

A scheme to account for the properties of various forms of oxy- and hydro-cellulose based on the study of these, several forms of which were prepd. and treated by a variety of methods, and the data are favorably compared with the degradation of cellulose. Hydrocellulose has a structure very similar to that of cellulose. At least 4 types of oxycellulose are distinguished. Fission to produce aldehyde and alc. groups, oxidation and reduction of terminal groups, estn. of chain length, etc., are compared to results of the usual methods of test and analyses in prepg. this scheme. (C)

Ozone: Role as Catalyst of Oxidation. E. Briner and G. Papazian. *Helv. Chim. Acta*, 1940, V. 23, P. 495–513, 542–548; abs. in *J. T. I.*, July 1940, V. 31, P. A415. (C)

The Peroxide Accumulation Rate of Oils—Relationship to Mackey Test Results and Oxidation on Textiles. W. Garner and M. Ellsworth. *Analyst*, V. 65, 347–51 (1940); cf. *C. A.*, V. 34, 4277; *Ibid.*, V. 34, Col. 5667.

When oils are added for fiber lubrication in wool combing, about 1 lb. of oil is spread over a max. surface of about 0.5 acre. The conditions are favorable to rapid oxidation which is necessary to produce fission products which are pale in color and easily scoured out but resinous or paint-like polymers are sometimes formed which are hard to remove and in some cases the oxidation is sufficiently rapid to cause spontaneous combustion of the oiled fibers. For textile and fire-insurance purposes it has been customary to use the Mackey test (*J. Soc. Chem. Ind.*, V. 15, 90 (1896) to det. whether an oil is suitable for textile purposes. The temp. rise in the Mackey app. is probably caused by peroxide formation and decompn. and the rate of accumulation of peroxides in an oil exposed to light and air should be a measure of the effective activity of the oxidizing catalyst content. An app. therefore has been devised to measure the peroxide accumulation rate (P. A. R.). Oil is placed in a shallow glass dish which is then exposed to the light from a 100-w. elec. lamp with the heat rays cooled by running water. The peroxides in 1 g. of the oil are detd. by Lea's method (*C. A.*, V. 25, 4424). From the results the following conclusions are drawn: (1) The rate of oxidation and the type of end product should be considered. The former depends upon the balance between catalyst and antioxidant and the latter upon the quantity of di- and poly-ethenoids present. (2) The P. A. R. values indicate the balance between catalyst and antioxidant; large values go with bad Mackey tests. (3) The P. A. R. does not give any reliable indication of the quantity of oxidizing catalysts present of the type of product formed by oxidation. (4) A high P. A. R. always indicates that an oil is unsuitable but a low P. A. R. does not always indicate suitability, because very unsatd. oils can be prepd. with low rates of oxidation. (5) The P. A. R. gives the same kind of information that the Mackey test does and is easier to carry out consistently. (6) The P. I. V. (peroxide I value) is useless for evaluating textile oils. (C)

THE PROPERTIES OF THE OXYCELLULOSES FORMED IN THE EARLY STAGES OF THE OXIDATION OF COTTON CELLULOSE BY PERIODIC ACID AND METAPERIODATE. G. F. Davidson. *J. T. I.*, July 1940, V. 31, P. T81–T96.

(1) The properties of oxycelluloses formed in the early stages of the oxidation of cotton cellulose by periodic acid and potassium metaperiodate have been studied and compared with those of other types of chemically modified cellulose previously examined. (2) Within the range of oxidative attack investigated (oxygen consumptions not exceeding one atom to every hundred glucose units), the copper number of the periodic acid oxycelluloses is proportional to the oxygen consumption. (3) The absorption of Methylene Blue by cotton cellulose is not appreciably affected by periodic acid oxidation within the stated range. (4) Periodic acid oxycelluloses exhibit the property of alkali-sensitivity in an extreme degree. As a result of treatment of the oxycelluloses with dilute alkalis their nitrocellulose fluidity (fluidity of derived nitrocelluloses in acetone solution) may be greatly increased and their tensile strength greatly diminished. (5) The nitrocellulose fluidity of a periodic acid oxycellulose is only slightly greater than that of the original cotton, and is thus much less than that of a hydrocellulose of equal cellulose fluidity (in cuprammonium solution); after alkali-boling, however, the periodic acid oxycelluloses show the same relation between cellulose fluidity and nitrocellulose fluidity as hydrocelluloses and alkali-boiled oxycelluloses of other types. (6) Periodic acid oxycelluloses resemble the dichromate oxycelluloses in being considerably stronger than hydrocelluloses of equal cellulose fluidity but after alkali-boiling the relation between cellulose fluidity and tensile strength is much more nearly the same for all these types of modified cellulose. (7) Periodic acid oxycelluloses are considerably weaker than dichromate oxycelluloses of equal nitrocellulose fluidity and the relation between the tensile strength and the nitrocellulose fluidity of modified celluloses varies with the method of modification more than was previously thought. (8) Oxidation of cotton cellulose by potassium metaperiodate solutions (pH 5.3) yields oxycelluloses which are indistinguishable from those produced by the action of periodic acid. (9) Evidence is adduced to show that the increase of nitrocellulose fluidity or fall of tensile strength produced by the action of alkalis on periodic acid oxycelluloses is not intimately connected with destruction of reducing groups which may accompany it. (10) The results which show the alkali-sensitivity of periodic acid oxycelluloses are interpreted as an indication of the presence in the oxidized chain-molecules of linkages that may be broken by alkalis. (C)

THE SIMILARITY OF CELLULOSE AND RUBBER AND THE FORMATION OF FIBERS OF ARTIFICIAL CELLULOSE AS A MACROMOLECULAR PROCESS. P. H. Hermans. *Naturwissenschaften*, V. 28, 223 (1940); abs. in *C. A.*, V. 34, Col. 6063. (C)

SOYBEAN PROTEIN DISPERSIONS: PREPARATION. A. K. Smith and H. J. Max. *Ind. Eng. Chem.*, 1940, V. 32, P. 411–415. (C)

SPECIFICATION FOR A TEXTILE OIL. W. Garner. *J. Soc. Dyers Col.*, Aug. 1940, V. 56, P. 333. (C)

STARCH: ZYMOLYSIS. Ch. Wunderly. *Helv. Chim. Acta*, 1940, V. 23, P. 414–428; abs. in *J. T. I.*, July 1940, V. 31, P. A408.

The author discusses the question whether one enzyme reaction can be influenced by another and gives experimental evidence in two directions. (C)

STRUCTURE OF THE COLLOIDAL MOLECULE AND STREAMING BIREFRINGENCE. C. Sadron. *J. chim. physique*, June 1939, P. 235–36; abs. in *Eastman Kodak Abs. Bull.*, June 1940, P. 337.

The value of streaming birefringence measurements in estimating the dimensions of large molecules and the dispersivity of solutions is indicated. (S)

A SURVEY OF ABRIDGED SPECTROPHOTOMETERS. J. A. Van den Akker. *Paper Trade J.*, 1940, V. 111, No. 11, P. 28–37.

A survey has been made of abridged spectrophotometers by the author, who is associated with the Institute of Paper Chemistry, Appleton, Wis., and a description and a discussion of the uses of these instruments are given. (C)

SURVEY OF SPECTROPHOTOMETERS. Kasson S. Gibson. *Paper Trade J.*, 1940, V. 111, No. 10, P. 33–37.

Reference is made to various previous surveys of spectrophotometry, and the present paper merely brings the subject up to date, with particular emphasis on reflection measurements. Visual spectrophotometric measurements have proved inadequate for the accurate colorimetric specification of white and near-white materials. The colors of such materials are importantly affected by small changes or differences of spectral reflection, differences that are of the order of magnitude of the uncertainties inherent in visual spectrophotometry. The photoelectric cell, on the other hand, is ideally adapted to the determination of small differences, and in apparatus designed on sound electrical and optical principles is capable of yielding spectrophotometric measurements that are both precise and accurate. All reflection spectrophotometers measure the apparent reflectance of a material relative to the apparent reflectance of a working standard, under certain fixed conditions of illumination and observation. The concept of apparent reflectance, the importance of considering the most desirable conditions of illumination and viewing, and the question of primary and secondary standards of apparent reflectance, are accordingly briefly considered. (C)

VISCOSE RAYON: STRUCTURAL RELATION TO NATURAL CELLULOSE FIBERS. J. Compton. *Ind. Eng. Chem.*, 1939, V. 31, P. 1250–9.

The author, an advocate of the dual concept of cellulose fibre structure ("crystalline microscopic ellipsoidal cellulose particles surrounded by a continuous intercrystalline material"), has made a study of the viscose process, using cotton fibres, linters and wood pulp as raw materials, measuring changes in viscosity (in cuprammonium) of the regenerated cellulose by means of capillary viscometers (B. C. I. R. A.; Ostwald; Fenske), and making photomicrographs (reproduced) and particle counts (with a Leitz slit ultramicroscope) at various stages. It is argued that the intercrystalline phase, but not the crystalline particle, is altered—in ageing by oxida-

tion and in sulphiding by disruption of the organized structure. Methods, and their limitations, of improving the physical properties of rayon are discussed. Molecular weight determinations on cellulose are considered and it is noted that, on the basis of the dual structure theory, determinations by other than purely chemical means have no real significance. (C)

VISCOSITY OF PRODUCTS OF FRACTIONING OF COTTON CELLULOSE. A. A. Morozov. *Colloid J.* (U. S. S. R.), 1939, V. 5, P. 691–706; abs. in *C. A.*, 1940, V. 34, Col. 1180. (C)

XANTHATION OF SODA CELLULOSE: RATE OF. Philip C. Scherer and K. T. Lin. Part I. *Rayon Text Mo.*, Aug., Sept. 1938; Part II. *Ibid.*, Jan., Feb., 1939. Part III. Distribution of Carbon Disulfide. *Ibid.*, 1939, Sept., P. 68–9; Oct., P. 57–60. (C)

X-RAY EXAMINATION OF DENITRATED FIBERS. T. Petitpas. *Mémorial des poudres*, 1939, V. 29, P. 195–96; abs. in *Eastman Kodak Abs. Bull.*, June 1940, P. 337.

As denitration proceeds, the diagram of the trinitrate is given down to 13.75% nitrogen, while the dinitrate diagram is given down to 11.3% nitrogen; the latter persists with contents greater than 9.5% nitrogen. (S)

X-RAY STUDIES OF CRYSTALLITE ORIENTATION IN CELLULOSE FIBRES. III. FIBRE STRUCTURES FROM COAGULATED CELLULOSE. Wayne A. Sisson. *J. of Phys. Chem.*, April 1940, V. 44, P. 513–529.

Earlier investigations regarding the orienting properties of native cellulose in both natural fibres and in synthetic fibres made from bacterial cellulose membranes have been extended to hydrate cellulose in synthetic fibres produced from cellulose coagulated from various solutions. The hydrate cellulose crystallite possesses a major orienting tendency with reference to the *b*-axis, and a minor or selective orienting tendency with reference to the 101 plant. Orientation of these axes may be produced either by shrinkage or by elongation of the sample. Whenever there is a relative increase in dimension of a sample in one direction, the *b*-axes of the unit cell tend to orient parallel to that direction; if there is a relative decrease in dimension in one direction, the 101 planes are oriented perpendicular to that direction. The degree of orientation in each case is proportional to the relative change in dimensions of the sample. In films such as Cellophane, the x-ray diagram shows a selective uniplanar orientation of the 101 plane if, upon drying, the swollen film is allowed to shrink only normal to the plane of the film. Likewise rayon fibres, especially viscose, if spun without tension, show a similar selective orientation with reference to the fibre surface. In both films and fibres, selective orientation of the 101 plane is destroyed by stretching, which produces a uniaxial orientation of the *b*-axis (axis of cellulose chains) parallel to the direction of stretching. (C)

X-RAY STUDIES REGARDING THE STRUCTURE AND BEHAVIOR OF NATIVE CELLULOSE MEMBRANES. Wayne A. Sisson. *Chem. Revs.*, April 1940, V. 26, P. 187–201. (C)